University Of Alberta
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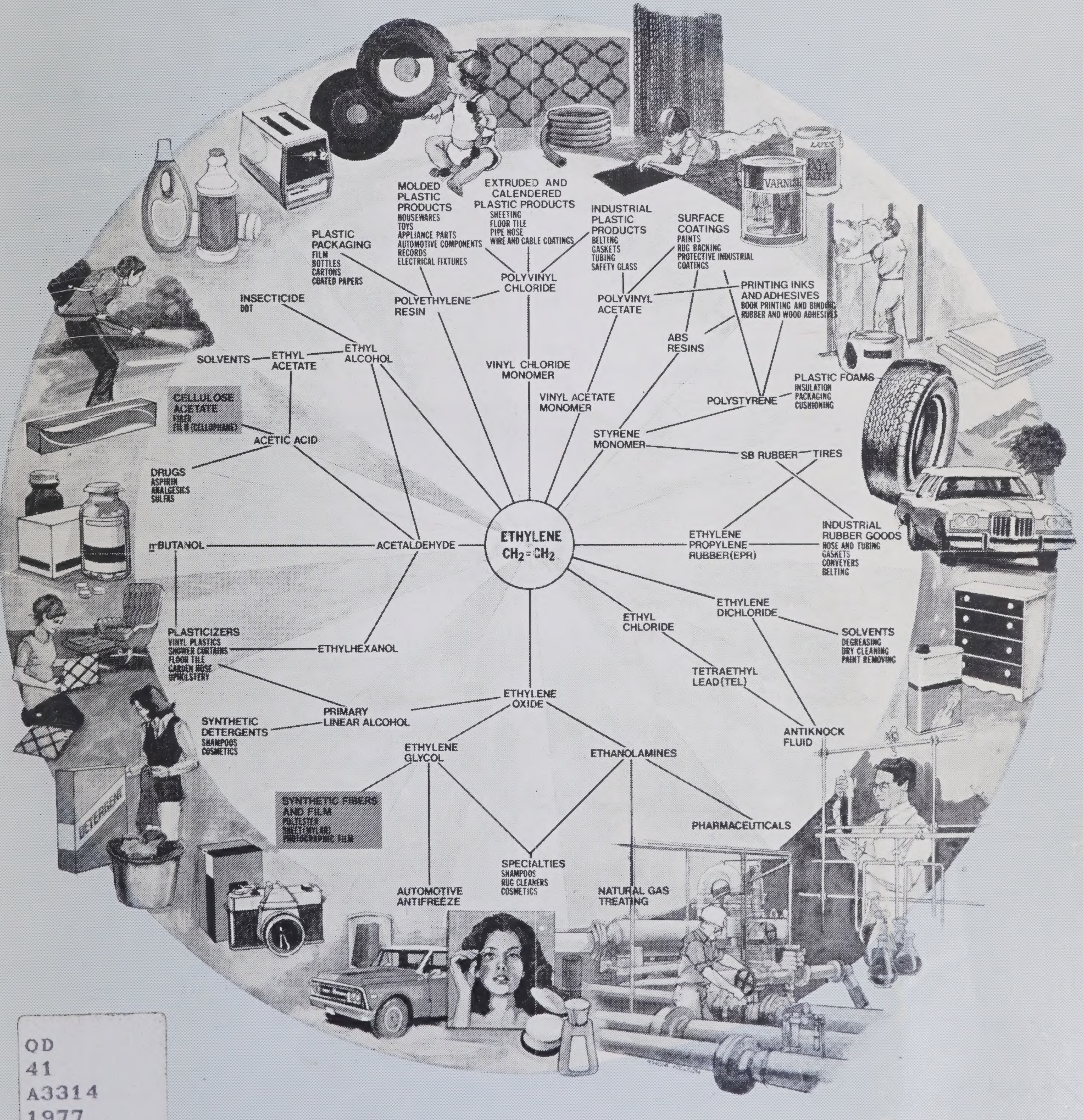
IYLENE and its DERIVATIVES



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ALCHEM

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1. Radioactive Isotopes

Isotope	Half-Life*	Decay Mode**	Isotope	Half-Life*	Decay Mode**
$^{3}_{1}H$	12.3 a	β^-	$^{216}_{84}Po$	0.160 s	α
$^{14}_{6}C$	5.77×10^3 a	β^-	$^{218}_{84}Po$	3.05 min	α, β^-
$^{24}_{11}Na$	15.0 h	β^-, γ	$^{220}_{86}Rn$	51.5 s	α
$^{32}_{15}P$	14.3 d	β^-	$^{222}_{86}Rn$	3.82 d	α
$^{30}_{16}S$	1.40 s	β^+	$^{224}_{88}Ra$	3.64 d	α
$^{36}_{17}Cl$	3.00×10^5 a	β^-	$^{226}_{88}Ra$	1.62×10^3 a	α, γ
$^{40}_{19}K$	1.30×10^9 a	β^-, γ	$^{228}_{88}Ra$	6.70 a	β^-
$^{45}_{20}Ca$	1.65×10^2 d	β^-	$^{228}_{89}Ac$	6.13 h	β^-
$^{60}_{27}Co$	5.27 a	β^-, γ	$^{228}_{90}Th$	1.91 a	α
$^{90}_{38}Sr$	28 a	β^-	$^{235}_{92}U$	7.13×10^8 a	α, γ
$^{131}_{53}I$	8.05 d	β^-, γ	$^{239}_{94}Pu$	2.44×10^4 a	α, γ
$^{212}_{82}Pb$	10.6 h	β^-	$^{242}_{95}Am$	16.0 h	α, β^-
$^{212}_{83}Bi$	60.6 min	α, β^-			
$^{212}_{84}Po$	3.00×10^{-7} s	α			

* s = seconds
min = minutes
h = hours
d = days
a = years

** α = alpha particle
β^- = beta particle
β^+ = positron
γ = gamma photon
α, β = alpha & gamma

2. Miscella

$\Delta H_{H_2O_{(s)} \rightarrow H_2O_{(\ell)}}$ = 6.03 kJ/

$\Delta H_{H_2O_{(\ell)} \rightarrow H_2O_{(g)}}$ = 40.8 kJ/mol

$c_{H_2O_{(s)}}$ = 2.01 J/(g·°C)

$c_{H_2O_{(\ell)}}$ = 4.19 J/(g·°C)

$c_{H_2O_{(g)}}$ = 2.01 J/(g·°C)

c = 3.00×10^8 m/s
e^- = q_{e^-} = 1.60×10^{-19} C
N = 6.02×10^{23}/mol
Q = 9.65×10^4 C/mol$_{e^-}$
1 C = 6.24×10^{18} e^-
*1 kW·h = 3.6 MJ
*1 atm = 101.325 kPa
*1 A = 1 C/s
*1 V = 1 J/C = 96.5 kJ/mol$_{e^-}$
*1W = 1 J/s
*1 t = 1000 kg = 1 Mg

* exact values

Chem

data sh et

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3. Atomic Molar Masses of Isotopes

$^{0}_{-1}e$ = 0.000 548 6
$^{1}_{1}p$ = 1.007 276 5
$^{1}_{0}n$ = 1.008 665 0
$^{1}_{1}H$ = 1.007 825
$^{2}_{1}H$ = 2.014 0
$^{3}_{1}H$ = 3.016 05
$^{3}_{2}He$ = 3.016 03

$^{4}_{2}\alpha$ = 4.001 50
$^{4}_{2}He$ = 4.002 60
$^{5}_{2}He$ = 5.012 3
$^{5}_{3}Li$ = 5.012 5
$^{12}_{6}C$ = 12 (exactly)
$^{14}_{7}N$ = 14.003 07
$^{15}_{7}N$ = 15.000 11

$^{16}_{8}O$ = 15.994 91
$^{35}_{17}Cl$ = 34.968 85
$^{56}_{26}Fe$ = 55.934 9
$^{206}_{82}Pb$ = 205.974 5
$^{210}_{84}Po$ = 209.982 9
$^{235}_{92}U$ = 235.043 9
$^{238}_{92}U$ = 238.050 8

4. Relative Strengths of Oxidizing and Reducing Agents

SOA

	**$E°$ (V)
$^{***}F_{2(aq)} + 2e^- \rightleftharpoons 2F^-_{(aq)}$	+2.87
$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightleftharpoons 4H_2O_{(\ell)} + Mn^{2+}_{(aq)}$	+1.49
$Au^{3+}_{(aq)} + 3e^- \rightleftharpoons Au_{(s)}$	+1.42
$^{***}Cl_{2(aq)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$	+1.36
$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 7H_2O_{(\ell)} + 2Cr^{3+}_{(aq)}$	+1.33
$N_2H^+_{5(aq)} + 3H^+_{(aq)} + 2e^- \rightleftharpoons 2NH^+_{4(aq)}$	+1.27
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(\ell)}$	+1.23
$2IO^-_{3(aq)} + 12H^+_{(aq)} + 10e^- \rightleftharpoons 6H_2O_{(\ell)} + I_{2(aq)}$	+1.19
$Br_{2(aq)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$	+1.09
$Hg^{2+}_{(aq)} + 2e^- \rightleftharpoons Hg_{(\ell)}$	+0.85
$2NO^-_{3(aq)} + 4H^+_{(aq)} + 2e^- \rightleftharpoons 2H_2O_{(\ell)} + N_2O^*_{4(g)}$	+0.81
$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2O_{2(\ell)}$	+0.68
$I_{2(aq)} + 2e^- \rightleftharpoons 2I^-_{(aq)}$	+0.54
$O_{2(g)} + 2H_2O_{(\ell)} + 4e^- \rightleftharpoons 4OH^-_{(aq)}$	+0.40
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$	+0.15
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$	0.00
$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)}$	-0.13
$Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)}$	-0.14
$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$	-0.23
$Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co_{(s)}$	-0.28
$Cd^{2+}_{(aq)} + 2e^- \rightleftharpoons Cd_{(s)}$	-0.40
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	-0.41
$Cr^{3+}_{(aq)} + 3e^- \rightleftharpoons Cr_{(s)}$	-0.74
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	-0.76
$2H_2O_{(\ell)} + 2e^- \rightleftharpoons 2OH^-_{(aq)} + H_{2(g)}$	-0.83
$2NO^-_{3(aq)} + 2H_2O_{(\ell)} + 2e^- \rightleftharpoons 4OH^-_{(aq)} + N_2O^*_{4(g)}$	-0.85
$SO^{2-}_{4(aq)} + H_2O_{(\ell)} + 2e^- \rightleftharpoons SO^{2-}_{3(aq)} + 2OH^-_{(aq)}$	-0.92
$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	-1.66
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$	-2.37
$Na^+_{(aq)} + e^- \rightleftharpoons Na_{(s)}$	-2.71
$Ca^{2+}_{(aq)} + 2e^- \rightleftharpoons Ca_{(s)}$	-2.76
$K^+_{(aq)} + e^- \rightleftharpoons K_{(s)}$	-2.92
$Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)}$	-3.04

Decreasing Strength of Oxidizing Agents

Decreasing Strength of Reducing Agents

SRA

* Colorless $N_2O_{4(g)}$ decomposes into brown $NO_{2(g)}$.

** Reduction potentials for 1.0 mol/L aqueous solutions at 25°C and 101 kPa.

*** Shown as aqueous for convenience; actually measured in gaseous form.

5. Molar Heats of Formation*

t = 25°C P = 101 kPa

Name	Formula	H_f (kJ/mol)
acetic acid	$CH_3COOH_{(\ell)}$	-488.6
acetone	$CH_3COCH_{3(\ell)}$	-115.6
acetylene	$C_2H_{2(g)}$	+226.9
aluminum oxide	$Al_2O_{3(s)}$	-1676.8
ammonia	$NH_{3(g)}$	- 46.1
benzene	$C_6H_{6(\ell)}$	+ 82.8
butane	$C_4H_{10(\ell)}$	-124.8
calcium carbide	$CaC_{2(s)}$	- 62.8
calcium carbonate	$CaCO_{3(s)}$	-1205.8
calcium chloride	$CaCl_{2(s)}$	-795.5
calcium oxide	$CaO_{(s)}$	-636.0
carbon dioxide	$CO_{2(g)}$	-393.6
carbon disulfide	$CS_{2(\ell)}$	+117.2
carbon monoxide	$CO_{(g)}$	-110.5
copper(II) oxide	$CuO_{(s)}$	-166.6
copper(I) oxide	$Cu_2O_{(s)}$	-155.3
ethane	$C_2H_{6(g)}$	- 84.6
ethanol	$C_2H_5OH_{(\ell)}$	-277.6
ethene (ethylene)	$C_2H_{4(g)}$	+ 52.3
ethylene dichloride	$C_2H_4Cl_{2(\ell)}$	-166.3
ethylene glycol	$C_2H_4(OH)_{2(\ell)}$	-455.0
ethylene oxide	$C_2H_4O_{(g)}$	- 51.1
glucose	$C_6H_{12}O_{6(s)}$	-900.0
hydrogen chloride	$HCl_{(g)}$	- 92.6
hydrogen iodide ($I_{2(s)}$)	$HI_{(g)}$	+ 26.0
hydrogen iodide ($I_{2(g)}$)	$HI_{(g)}$	- 5.0
hydrogen peroxide	$H_2O_{2(\ell)}$	-188.0
hydrogen sulfide	$H_2S_{(g)}$	- 20.5
iron(III) oxide	$Fe_2O_{3(s)}$	-822.7
methane	$CH_{4(g)}$	- 74.9
methanol	$CH_3OH_{(\ell)}$	-238.6
nitrogen dioxide	$NO_{2(g)}$	+ 33.9
nitrogen monoxide	$NO_{(g)}$	+ 90.4
nitromethane	$CH_3NO_{2(\ell)}$	- 89.2
octane	$C_8H_{18(\ell)}$	-208.7
propane	$C_3H_{8(g)}$	-103.8
sucrose	$C_{12}H_{22}O_{11(s)}$	-1742.0
sulfuric acid	$H_2SO_{4(\ell)}$	-812.2
sulfur dioxide	$SO_{2(g)}$	-297.3
2,2,4-trimethylpentane	$C_8H_{18(\ell)}$	-224.6
sulfur trioxide	$SO_{3(g)}$	-396.1
vinyl chloride	$C_2H_3Cl_{(g)}$	+ 33.9
water (liquid)	$H_2O_{(\ell)}$	-286.0
water (vapor)	$H_2O_{(g)}$	-242.0

* *Molar heats of formation for elements in natural occurring form are assumed to be zero.*

Refer to the *CRC Handbook of Chemistry and Physics* for further data.

Side 1

LIBRARY
UNIVERSITY OF ALBERT

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PREFACE

Introduction

ALCHEM is the result of many educators joining together to write and teach a chemistry program that would meet the needs of todays students. Through six years of classroom experimentation with over 50 000 students, the program has come to its present form. In answer to the request made by teachers and students throughout the country, ALCHEM has become the most descriptive and applied chemistry material available on the market today.

This approach of applied and descriptive chemistry is integrated into the textual material, labs, demonstrations and classroom exercises to an extent never done before. Environmental, consumer and industrial chemistry are found throughout the program as well as many historical references and biographies on famous chemists. All this has been achieved without sacrificing a high level of chemistry. The chemistry content is not watered down. You will see from the unique design of the format, that the material has an easy-to-learn-from classroom approach. Students like using the program and their achievement level is high. Test results prove that ALCHEM students have significantly outperformed students on other programs and they have shown an equal or higher interest in chemistry.

Organization of the Program

In its present form there are three core books, ALCHEM 10, ALCHEM 20 and ALCHEM 30, which can be used for two half-courses and one full course, respectively, or with two full courses. Each core book is divided into units that cover specific topics. Within each unit, labs, demos and exercises are integrated in a logical sequence with the textual material. The ALCHEM 20 and 30 each have a complete review unit that acts as a refresher for the student who may not be familiar with previous content. It is our experience that a student can begin the program quite easily even if he or she starts with ALCHEM 30. Each core book can stand on its own.

In addition to the three core books, seven elective units are available to give added dimension to special topics selected by students or teachers. The core units emphasize the concepts of chemistry and bring in the applied and descriptive chemistry where possible. The elective units emphasize the applied and descriptive chemistry and bring in the concepts of chemistry where possible. There is a balance of organic and inorganic electives. The elective units are; *Foods and Their Analogs, Athabasca Tar Sands, Analytical Chemistry, Nuclear Chemistry, Metallurgy and Corrosion, Ethylene and its Derivatives,* and *Alberta Chemical Industries.*

The strongest feature in the whole program is that all the material has been reworked and revised many times to make it pedagogically sound for both the student and the teachers. Many new ways of approaching traditionally difficult chemistry concepts have resulted in the student finding the new approaches easy to understand. For example, the *Gravimetric Stoichiometry* unit is prepared for so thoroughly in the earlier units that it becomes a summary unit. Seven types of bonding in the *Chemical Bonding* unit are explained simply in terms of simultaneous attractions. All questions in the *Energy* unit are done by the approach of heat lost equals heat gained. All redox and acid-base reactions are done by a single five step method.

Another strong feature is the format. In many respects the teacher preparation time has been redirected. The students have the complete program in front of them in their loose leaf binders. Prepared exercises for the student to complete are placed next to the topic covered. Here the organization of the material minimizes the students confusion found in the use of other textbooks. The format of the exercises makes it easier for the teachers to concentrate on classroom strategies. Because quality classroom activities are already developed in the core material and the electives, the teacher has more time to devote to class and individual questions, implementing a wider variety of teaching strategies, spending more professional time on test making and reading, and preparing elective materials.

In addition to the above mentioned texts, an ALCHEM periodic table is available within each core book. Periodic table wall charts are also available. ALCHEM 30 includes the ALCHEM data sheet. Test item banks are available for ALCHEM 10, 20 and 30.

Special Features

The ALCHEM material was developed by the authors in consultation with science curriculum advisors in both education and chemistry at the University of Alberta. Through the years of piloting, many of the authors and pilot teachers devoted much of their free time and expertise to the improvement and enjoyment of their profession by producing a better chemistry program. ALCHEM serves as a model to what can be accomplished through local curriculum development projects. It also shows what dedicated classroom teachers can do, for without them, we would not have this classroom oriented approach. The over 120 pilot teachers that worked with the program, contributed feedback that is not normally found in other textbook projects. Their comments and criticisms helped make the material work better in the classroom.

For those concerned about the rising cost of textbooks, the ALCHEM prices are very reasonable. In fact, the ALCHEM program costs less than the conventional textbook program even if you amortize the costs of the conventional text over a three to five year period.

The illustrations are of a comic nature to add some fun and enjoyment to the serious chemistry topics. They are designed to bring humor into the classroom—to let the student feel that chemistry does not have to be a heavy subject.

The United States National Institution of Education Curriculum Development Task Force has found that a major reason for the failure of million dollar curriculum projects in the past, has been the lack of significant participation by classroom teachers. ALCHEM is successful because classroom teachers created the program and students find it to be an enjoyable and rewarding learning experience.

The Symons Report has stated that, "A curriculum in this country that does not help Canadians in some way to understand the physical and social environment in which they live and work...cannot be justified in either academic or practical terms. It is essential, from the standpoint of both sound balanced scholarship and of practicality, that studies of the Canadian situation occupy an appropriate place in the curriculum...". ALCHEM is an example of a program that fulfills many of the recommendations made in the Symons Report. ALCHEM is truly a Canadian science program.

The major recommendation of the International Conference on New Directions in Chemistry Curriculum held in 1978 at McMaster University stated that a greater proportion of applied and descriptive chemistry be integrated into chemistry core and elective curriculums and textbooks. In order to accomplish this addition some of the most theoretical topics have to be cut. ALCHEM serves as a unique example of how the applied and descriptive chemistry can be integrated into curriculum materials.

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ALCHEM MATERIALS

ALCHEM 10

Unit A: Elements and the Periodic Table
Unit B: Compounds, Bonding and Nomenclature
Unit C: Chemical Reactions
Unit D: The Mole
Unit E: Gravimetric Stoichiometry

ALCHEM 20

Unit F: Review of ALCHEM 10
Unit G: Chemical Bonding
Unit H: Organic Chemistry
Unit I: Solutions

ALCHEM 30

Unit K: Review of ALCHEM 10 & 20
Unit L: Energy
Unit M: Electrochemistry
Unit N: Acids and Bases

ALCHEM Electives (Available separately) (level)

Unit J: Analytical Chemistry (20, 30)
Unit O: Foods and Their Analogs (30, 20)
Unit - The Athabasca Tar Sands (30, 20)
Unit P: Ethylene and its Derivatives (30)
Unit S: Alberta Chemical Industries (10)
Unit T: Metallurgy and Corrosion (30)
Unit U: Nuclear Chemistry (30, 20)

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"MARVIN" The ALCHEM Mole

Other ALCHEM Materials

1. ALCHEM 10 Teachers' Guide
2. ALCHEM 20 Teachers' Guide
3. ALCHEM 30 Teachers' Guide
4. ALCHEM Electives Teachers' Guide
5. ALCHEM periodic table (student)
6. ALCHEM 30 data sheet (student)
7. ALCHEM 10 Test Item Bank (1979)
8. ALCHEM 20 Test Item Bank (1979)
9. ALCHEM 30 Test Item Bank (1979)
10. ALCHEM periodic table (wall chart) - Side 1 (1979)
11. ALCHEM periodic table (wall chart) - Side 2 (1979)
12. ALCHEM 30 data sheet (wall chart) - Side 1 (1979)
13. ALCHEM 30 data sheet (wall chart) - Side 2 (1979)

Prerequisite Knowledge and Skills

Before beginning the *Ethylene and its Derivatives* unit, the student should be able to (in decreasing order of importance):

1. draw Lewis (electron dot) diagrams and structural formulas for molecules
2. name and draw structural formulas for alkanes, alkenes, alkynes, aromatics, alcohols, carboxylic acids, esters and alkyl halides
3. write equations (using structural formulas) for substitution, addition, combustion, esterification and other organic reactions
4. determine heats of reactions from molar heats of formation
5. predict relative boiling points and solubilities based on dipole interactions, London dispersion forces and/or hydrogen bonding.
6. use Le Chatelier's Principle to predict changes in equilibrium conditions
7. operate a bunsen burner

Numbers 4, 5 and 6 are not required for many questions. These questions could be omitted without losing much continuity.

Unit Objectives

Upon completion of the Ethylene and its Derivatives unit, the student should be able to:

P1. differenciate between naphtha and ethane cracking methods of producing ethylene

P2. list the production pathway for end-products such as polyethylene, polyvinyl chloride, ethylene glycols, and ethanolamines

P3. write formulas for and name the major chemicals studied in the unit

P4. list the major components of natural gas

P5. explain the physical properties (i.e., melting point, boiling point, hardness and solubility) of major chemicals studied in the unit

P6. explain how ethane is extracted from natural gas

P7. list four ways of producing ethylene

P8. use molar heats of formation to determine molar heats of reactions for reactions in the unit

P9. perform stoichiometry problems involving reactions in the unit

P10. explain, provide examples of and differenciate between free radical and cationic polymerization

P11. list or recognize uses for the major chemicals studied in the unit

P12. explain the use of ethylene glycol as an antifreeze

P13. list the major methods for differenciating between plastics

ETHYLENE AND ITS DERIVATIVES
INTRODUCTION

Petrochemicals

Petrochemicals may be defined as chemicals which are derived from natural gas, crude oil, oil sands, oil shales, coal or manufactured gases and liquids. To qualify as a petrochemical the derived product must be used for something other than a fuel. About 300 new petrochemical products are introduced each year. Of the half million known petrochemicals only about three percent have been developed for use.

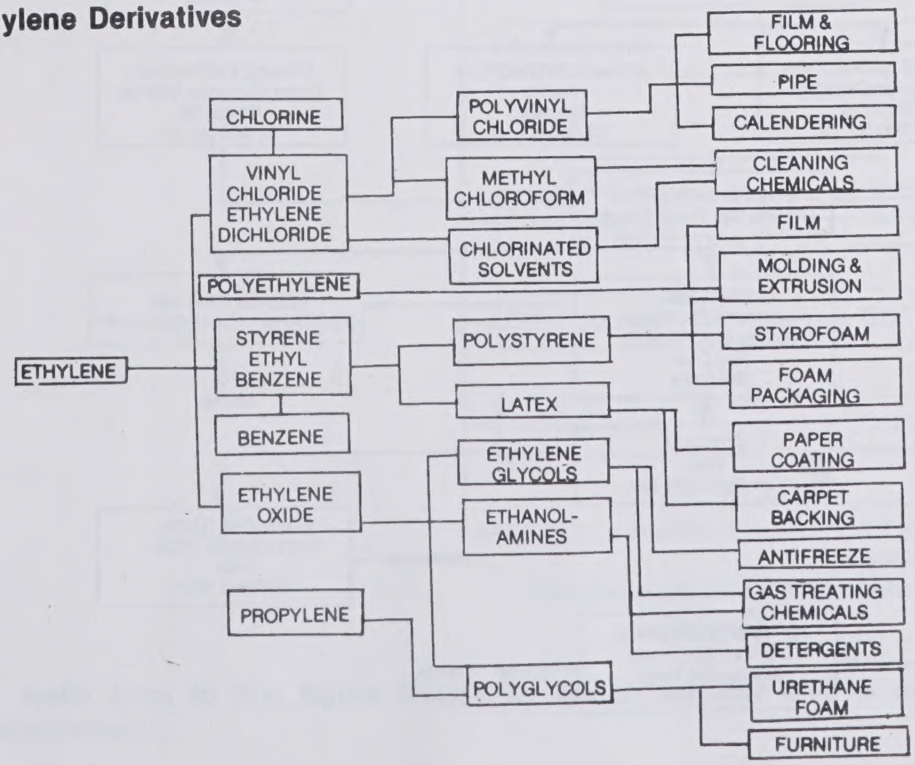
History of the Petrochemical Industry

The widespread use of the automobile led directly to the establishment of a petrochemical industry. The production of gasoline for the automobile gave as byproducts such petrochemicals as ethylene, propylene and butylenes. The search for a permanent (less volatile) antifreeze to replace ethanol resulted in the large scale production of ethylene glycol from ethylene in the 1920's. The requirement of an antiknock additive for automotive gasoline was satisfied by tetraethyl lead (produced from ethylene). The desire for self-sufficiency in rubber, in countries like Germany, Britain, U.S.A. and Canada around World War II, resulted in the production of synthetic rubbers from ethylene, benzene, butadiene and acrylonitrile.

Canada's petrochemical industry got its start during World War II when natural rubber supplies were cut off. The Polysar Corporation was established by the Canadian government and a synthetic rubber plant was built at Sarnia, Ontario. The rubber plant was built and run by a consortium of major rubber manufacturers although the plant was owned by Polysar (*poly* for polymer and *sar* for Sarnia). Feedstock for the synthetic rubber plant was supplied by the adjacent Imperial Oil refinery and the Dow Chemical styrene plant. After the war, in 1947, Dow Chemical of Canada built a Styron (polystyrene) plant near the Polysar plant. Dow used excess styrene from the Polysar synthetic rubber plant to produce the polystyrene. In 1948 Dow also opened an ethylene glycol plant using excess ethylene from the Polysar plant.

This initial activity was followed by a series of other petrochemical plants in Sarnia's *Chemical Valley*. Ethyl Corporation built a plant which used ethylene to produce tetraethyl lead (the anti-knock gasoline additive). Imperial Oil built three more plants—a detergent alkylate plant to produce synthetic soap, a cracking plant to produce ethylene, propylene, butylenes and butadiene, and an aromatics plant to produce benzene, toluene and xylene. DuPont built a polyethylene plant. Dow Chemical built facilities to produce caustic soda, styrene, ethylene, chlorine, hydrochloric acid and ammonia. The list of petrochemical plants at Sarnia has continued to grow and will continue to grow.

Ethylene Derivatives



ETHYLENE AND ITS DERIVATIVES
INTRODUCTION

Alberta's Petrochemical Industry

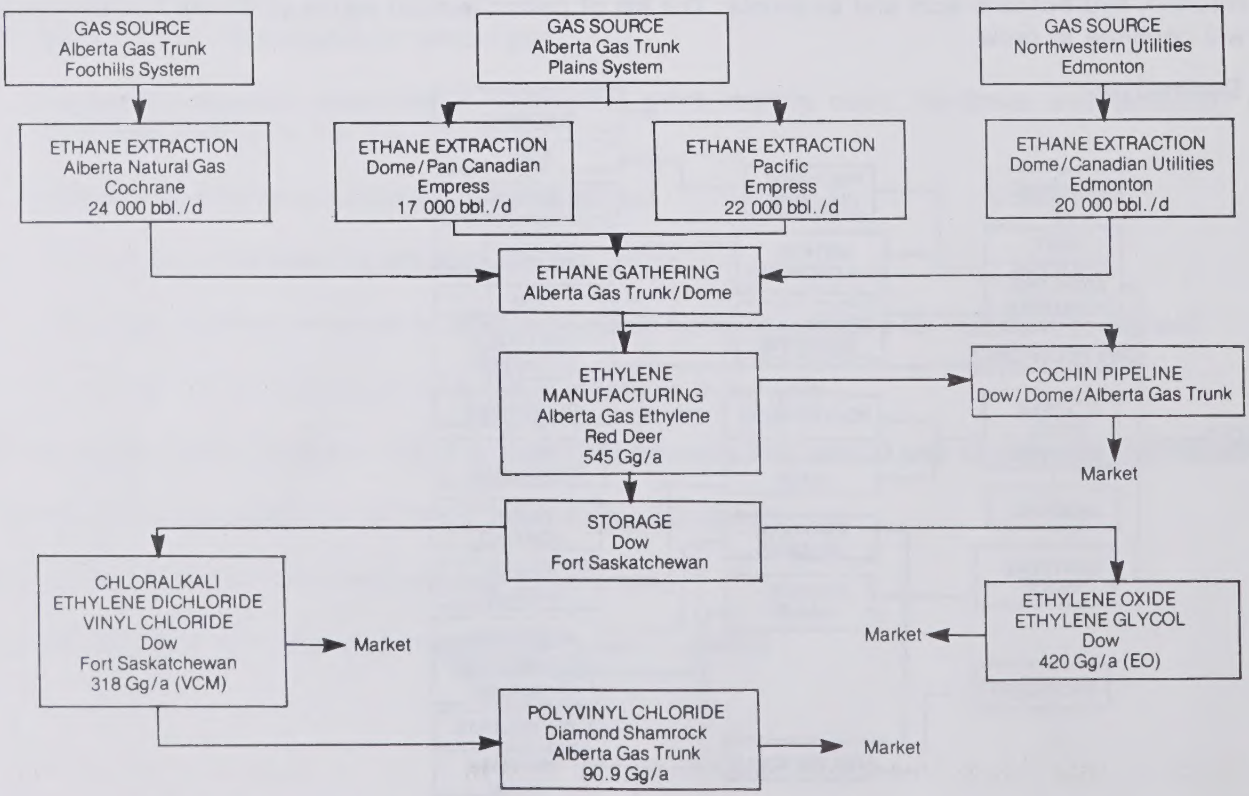
Thirty years after the establishment of the Sarnia petrochemical complex, a similar petrochemical building boom is occurring in Alberta. The initial construction of the major plants spanned the years 1977-1979. The first plants necessary were those to extract ethane from natural gas. Dome Petroleum built ethane extraction units at Edmonton and Empress. Pacific Petroleum and Alberta Natural Gas built ethane extraction units at Empress and Cochrane, respectively. The four plants supply ethane to the ethylene plant built by Alberta Gas Ethylene Company (AGEC) near Red Deer. Of the over one-half million kilograms of ethylene (ethene) produced by AGEC about 60 percent is consumed industrially in Alberta. The excess ethane and ethylene are shipped as liquids via pipeline to export markets in the U.S.A. and Eastern Canada. In Alberta the ethylene is converted by Dow Chemical into ethylene oxide and vinyl chloride at Fort Saskatchewan. The ethylene oxide is used by Dow to produce ethylene glycols. The vinyl chloride is partially consumed by Diamond Shamrock-Alberta Gas to produce polyvinyl chloride. The ethylene glycols and the polyvinyl chloride plants are situated at Fort Saskatchewan. The above covers the new major ethylene-related petrochemical complex in Alberta. The potential for expansion of this petrochemical area in Alberta (like at Sarnia) is now there.

Petalta (a partially owned subsidiary of the province owned Alberta Energy Company) built a benzene plant near Fort Saskatchewan. The opportunity now exists (if the markets are there) for building styrene and polystyrene plants. These latter plants would consume ethylene and benzene. Plans by Canadian Industries Limited (CIL) and DuPont for building polyethylene plants near Fort Saskatchewan and Red Deer, respectively, have been dropped due to lack of markets.

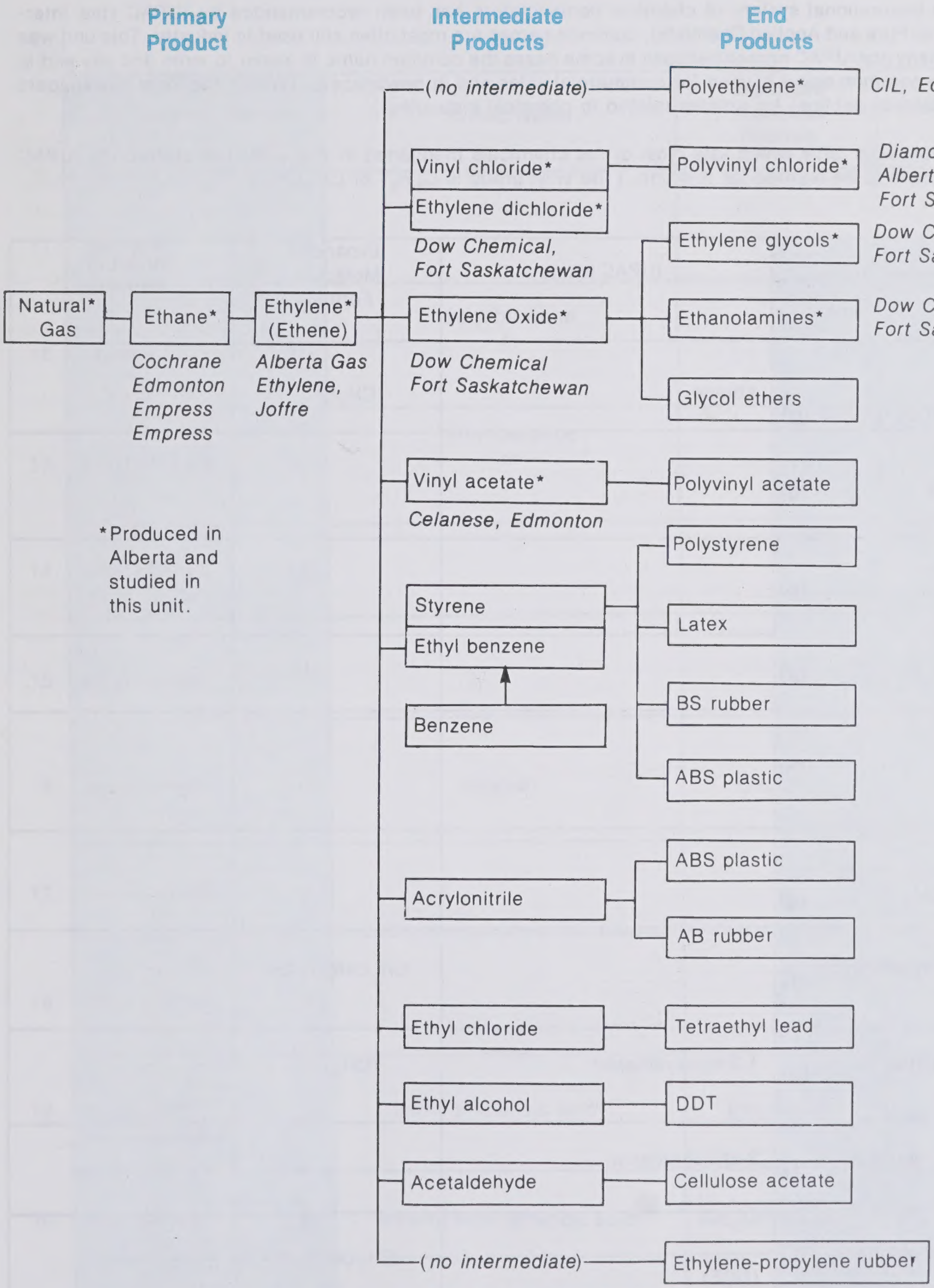
CIL has operated a polyethylene plant in Edmonton since 1953. However, the CIL plant did not form part of the new ethylene-related petrochemical complex. CIL extracts their own ethane from natural gas, produces their own ethylene and uses the ethylene to produce polyethylene (all on a small scale compared to newer world scale plants).

There are other chemical industries in Alberta which qualify as being called petrochemical industries. These industries, however, are not ethylene related. Only ethylene related petrochemical industries will be described in this unit. (The ALCHEM elective unit *Alberta's Chemical Industries* describes the chemistry of the other petrochemical industries in Alberta.)

Alberta Petrochemical Complex



ETHYLENE AND ITS DERIVATIVES
INTRODUCTION



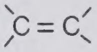
Ethylene and its Derivatives
Figure P1

Refer back to this figure frequently throughout the unit in order to trace the production of each end-product.

ETHYLENE AND ITS DERIVATIVES
INTRODUCTION

Although an international system of chemical nomenclature has been recommended by IUPAC (the International Union of Pure and Applied Chemists), common names are most often still used in industry. This unit was written using many nonIUPAC names because in some cases the common name is easier to write and say and in most cases the common name is used for commercial sales and in newspapers. (Watch the local newspapers (usually the business section) for articles related to chemical industries.)

Complete the following table which lists most of the chemicals mentioned in this unit. The starred (*) IUPAC names do not have to be learned for this unit. (The vinyl group is C_2H_3- or CH_2CH-.)

	Common Name (state)	IUPAC Name	Expanded Molecular Formula	Structural Formula
e.g.	ethylene *(accepted by IUPAC)* **(g)**	ethene	CH_2CH_2	
1.	propylene **(g)**			
2.	butylenes **(g)**			
3.	**(g)**			
4.	ethane **(g)**			
5.	vinyl chloride (monomer) (VC or VCM) **(g)**			
6.	(mono)ethylene glycol (MEG) **(*l*)**		CH_2OHCH_2OH	
7.	ethylene oxide (EO) **(g)**	1,2-epoxyethane*	$(CH_2)_2O$	
8.	ethylene chlorohydrin (ECH) **(*l*)**	2-chloroethanol		
9.	ethylene dichloride (EDC) **(*l*)**	(DCE)	CH_2ClCH_2Cl	
10.	(mono)ethanolamine (MEA) **(*l*)**	2-hydroxyethylamine* 2-aminoethanol*	$H_2NCH_2CH_2OH$	

ETHYLENE AND ITS DERIVATIVES
INTRODUCTION

	Common Name (state)	IUPAC Name	Expanded Molecular Formula	Structural Formula
11.	benzene (*l*)			
12.	styrene (*l*)	vinyl benzene or		
13.	ethyl benzene (*l*)	ethyl benzene or		
14.	ethyl chloride (g)			
15.	ethyl alcohol (*l*)			
16.	acetaldehyde (*l*)	ethanal*	CH_3CHO	
17.	methyl alcohol (*l*)			
18.	tetraethyl lead (*l*)			
19.	acrylonitrile (vinyl cyanide) (*l*)	nitrite propenoic acid*	CH_2CHCN	
20.	vinyl acetate (*l*)	ethenyl ester ethanoic acid*	$CH_2CHOOCCH_3$	
21.	natural gas (g)	(major component)		

Refer back to this page when new names or formulas are introduced in the unit. Note the state of matter and try to think of these substances as being in either the liquid or gas state.

ETHYLENE AND ITS DERIVATIVES
ETHYLENE FROM NAPHTHA

Introduction

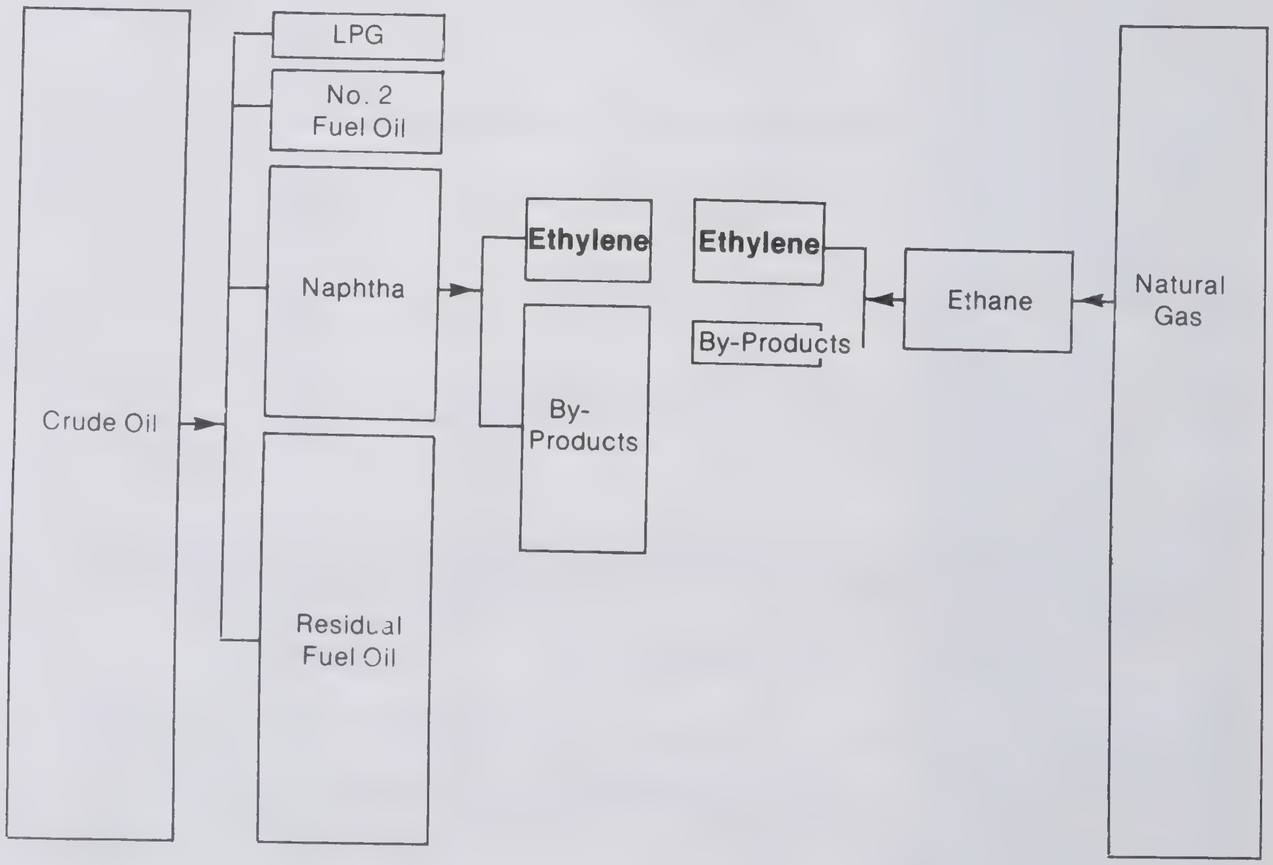
Ethylene (ethene) may be prepared from cracking either naphtha, a mixture of liquified petroleum gases, LPG, or ethane. Naphtha is a hydrocarbon mixture (C_4 to C_6 or C_7), obtained from crude oil feedstock. The ethane used to prepare ethylene is about 98% pure and is obtained from natural gas feedstock. The chosen method of producing ethene depends on the availability of feedstock and on the ease of marketing the by-products.

The Petrosar plant (1978) at Sarnia, Ontario produces ethylene from naphtha obtained from crude oil from Alberta. An established market and distribution system exists in Ontario for the by-products of naphtha production and its conversion to ethane.

Ethylene From Naphtha Cracking

The major method of producing ehtylene in the U.S.A. is by ethane cracking. In Europe and Japan the preferred process is naphtha cracking. In Canada the number of each type of process is about half and half. Petrosar (a consortium of the Federal crown corporation of Polysar, Canadian Development Corporation, Dupont and Union Carbide) has a world-scale naphtha cracking plant at Sarnia, Ontario which produces 455 Gg/a (455 million kilograms per year) of ethylene. Alberta Gas Ethylene Company (AGEC) (a wholly owned subsidiary of Alberta Gas Trunk Line (AGTL)) has a world-scale ethane cracking plant near Red Deer, Alberta which produces 545 Gg/a (545 million kilograms per year) of ethylene.

As mentioned earlier the naphtha cracking depends on naphtha feedstock from the refining of crude oil and the process produces large quantities of by-products which must be marketed. Figure F2 illustrates the relative quantities of feedstock and by-products to produce an equal amount of ethylene from naphtha and ethane cracking.



An Equal Amount of Ethylene From Naphtha vs Ethane Cracking
Figure P2

Ethane From Natural Gas

The Alberta Gas Ethylene Company (AGEC) plant (1979) near Red Deer, Alberta produces ethylene from ethane extracted from natural gas. In Alberta the choice of method for producing ethylene is obvious. Alberta produces, consumes and exports large quantities of natural gas. The ethane in the natural gas was previously burned as fuel as a component of the natural gas. Now the ethane is extracted from the natural gas in Alberta before the natural gas is consumed in Alberta or shipped via pipeline to the U.S.A. and Eastern Canada. The natural gas from the Canadian North (i.e., the Mackenzie Delta and the Beaufort Sea) will also pass through Alberta for distribution. Ethane could be extracted from this northern gas as well.

Not only does the large supply of natural gas in Alberta yield ethane but it also yields supplies of fuel needed for petrochemical plants. Another factor which dictated ethylene production from ethane rather than naphtha is the lack of markets for naphtha by-products in Alberta.

Natural Gas

Raw natural gas contains light hydrocarbons plus impurities such as condensates, water and in some cases hydrogen sulfide gas. These impurities must be removed before the gas may be used for whatever purpose. Gas processing plants must be located near the gas wells since the condensates could very quickly clog a pipeline. The pipelines from the gas wells to the processing plants must be heated and short to prevent condensation and further formation of condensates.

At the gas processing plant the condensates and the water are removed. At over forty plants in Alberta the hydrogen sulfide is removed from the *sour* natural gas (*sour* refers to the $H_2S_{(g)}$) to produce *sweet* process gas for the market place. For further information on sulfur and water extraction from natural gas see the ALCHEM unit, *Athabasca Tar Sands*, and the discussion of ethanolamines and ethylene glycols later in this unit.

The raw (sour) gas and the process (sweet) gas have varying composition depending on the gas field or even on the gas well within a field.

Table P1
Typical Composition of Process Gas

Component	Mole %	Component	Mole %
nitrogen	2.70	butane	0.15
carbon dioxide	0.34	2-methylpropane	0.09
methane	83.64	pentanes	0.08
ethane	11.64	hexanes	0.07
propane	1.75		

The sweet natural gas is either consumed in Alberta or is exported to the rest of Canada or the U.S.A. Some gas processing plants remove the propane, butane and pentane-plus or propane-plus fractions from the natural gas. (*Propane-plus* includes propane plus other hydrocarbons.) The ethane was not removed because of the further expense and the lack of a large market for the ethane. In the past the ethane was left in the natural gas and was burned as a fuel.

Ethane Extraction from Natural Gas

Older methods of removing liquified petroleum gases (LPG) from natural gas involved the absorption or dissolving (under high pressure) of the LPG in oil. Each LPG is sequentially removed from the oil by a controlled decrease of pressure and increase of temperature. The small amount of ethane absorbed is separated first and then is burned as a fuel at the plant. Only a small percentage of the ethane is actually removed. The other LPG's (nearly all absorbed) are separated as propane, butane, pentane-plus and/or propane-plus fractions by distillation. Each plant varies its process according to the markets it has.

With the introduction of a market for ethane, the absorption-by-oil process was either replaced or supplemented. The process which is necessary to the ethane extraction involves the cooling and compression of natural gas to condense the LPG from the gas phase into the liquid phase.

As indicated in Table P1, natural gas is a mixture of alkanes. Each of these alkanes has a different boiling point. The boiling points of the eight simplest alkanes are given in Table P2.

Table P2
Boiling Points of Simple Alkanes

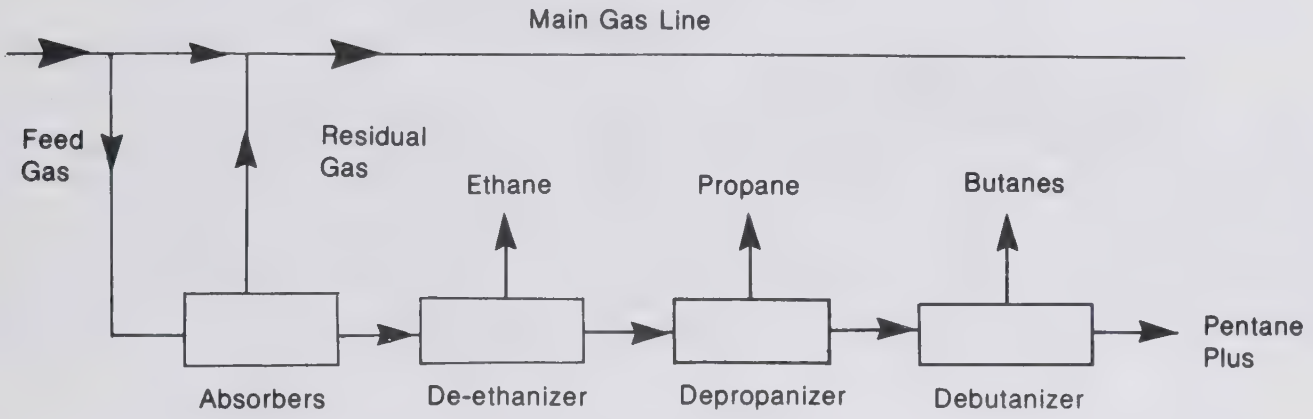
Alkane	Boiling Point (°C)	Alkane	Boiling Point (°C)
methane	-162	butane	0
ethane	-89	2,2-dimethylpropane	10
propane	-42	2-methylbutane	28
2-methylpropane	-12	pentane	36

The lower the boiling point (and consequently the smaller the intermolecular attractions), the greater is the difficulty in condensing the gas. Condensation of the gases (other than the unwanted methane) from the natural gas is achieved by low temperatures (down to -100 °C) and high pressures (1500 to 5000 kPa or 15 to 20 atmospheres).

The condensation method may be used by itself to remove all of the LPG or the condensation method may be used to further process any gases not absorbed by an oil absorption unit at a plant.

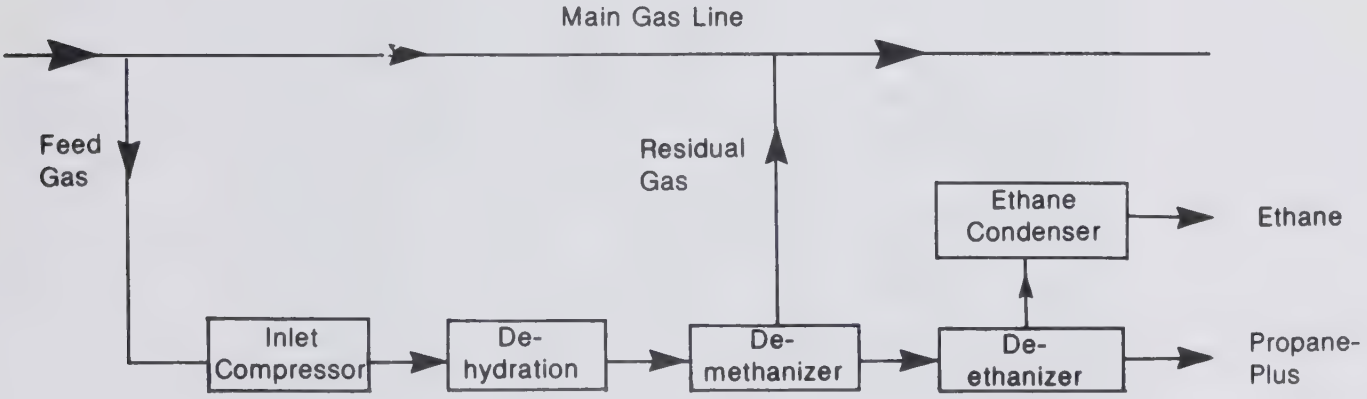
The introduction of a market for ethane (both inside and outside of Alberta) has resulted in the construction or expansion of four ethane extraction plants in Alberta. (See Figure P5.)

1. Dome/Canadian Utilities' 20 thousand barrels per day plant at Edmonton, Alberta
2. Dome/Pan-Canadian's 17 thousand barrels per day plant at Empress, Alberta
3. Pacific's 22 thousand barrels per day plant at Empress, Alberta
4. Alberta Natural Gas's 24 thousand barrels per day plant at Cochrane, Alberta.



LPG Absorption Plant
Figure P3

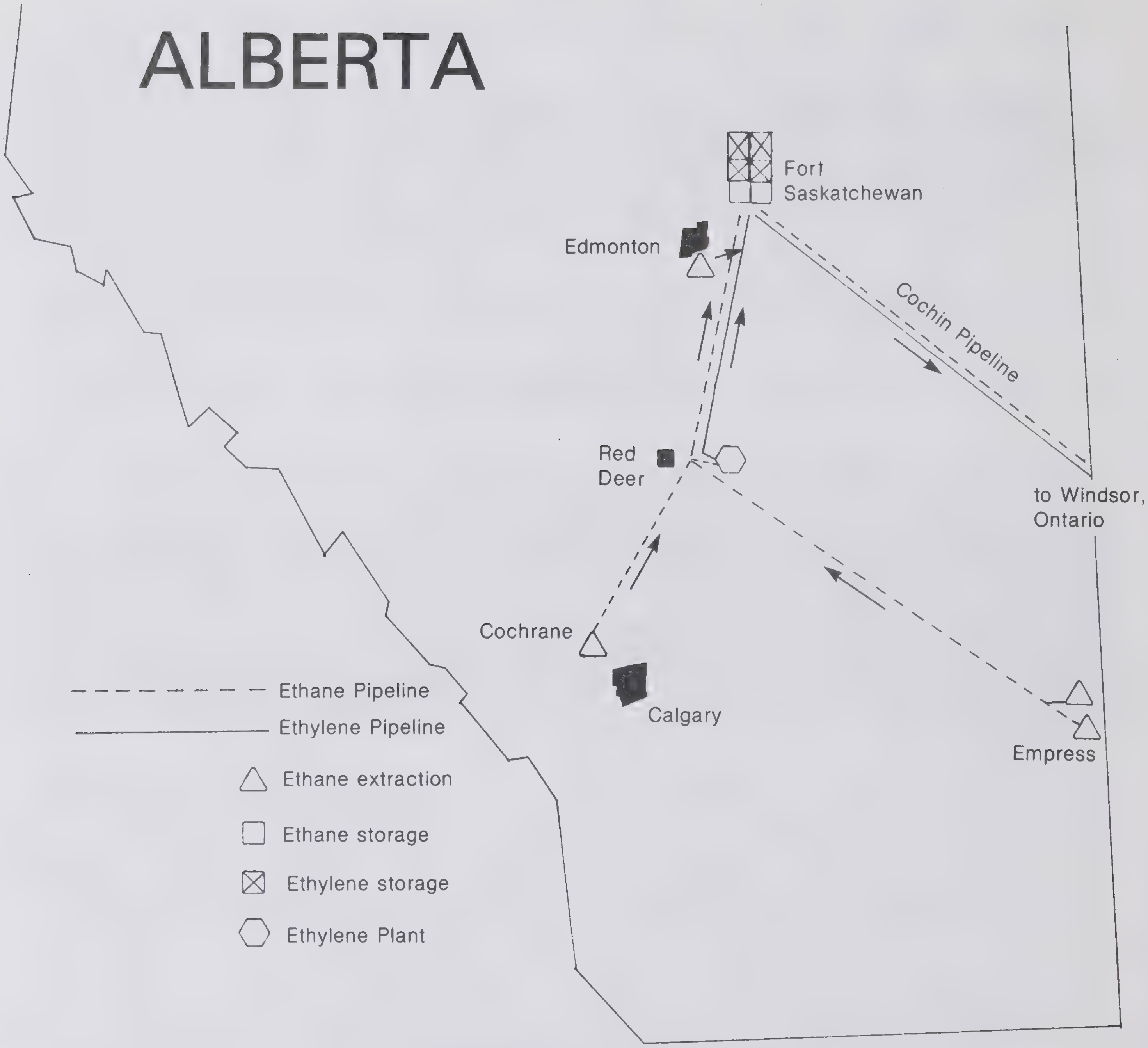
The percentage recovery of the ethane is very low in an absorption plant. Ethane that is absorbed must be removed in order to meet purity specifications for propane. The removed ethane is generally used as a fuel at LPG absorption plants.



LPG Condensation Plant
Figure P4

The recovery of the ethane from natural gas by a LPG condensation plant can economically be up to 90 percent efficient. The residue gas leaving the plant contains from 1 to 1½ percent ethane. In order to get better recovery the complete gas stream (including methane) would have to be condensed. The cost of complete condensation would exceed the financial return.

The propane-plus in Figure P4 can be fed to a pipeline for further fractionation elsewhere and/or it can be fractionated at the ethane extraction plant site. The liquified ethane is piped (under pressure) to markets inside and outside of Alberta.



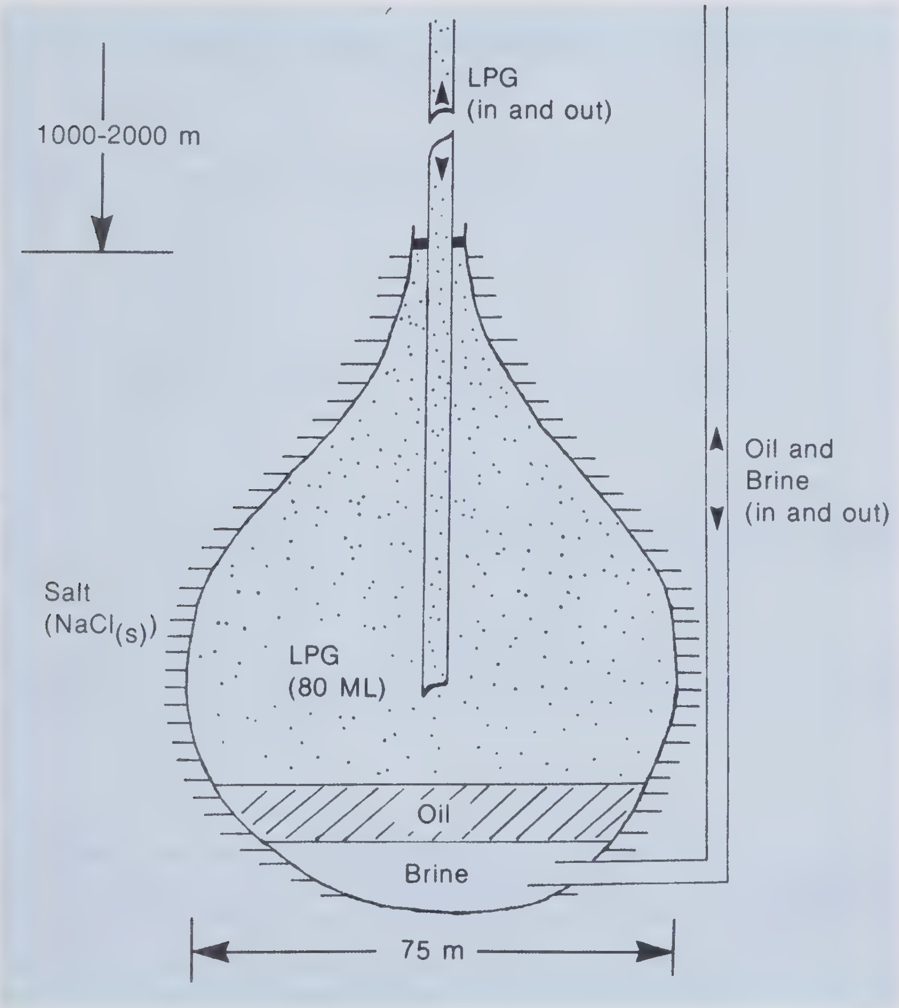
Ethane Distribution and Storage in Alberta
Figure P5

Ethane Distribution and Storage

About half of the ethane produced by the four ethane plants is consumed in Alberta by the AGEC ethylene plant near Red Deer. Ethane in liquid form is piped from Cochrane and Empress to AGEC. Excess ethane from AGEC is piped to Dome's two underground ethane storage caverns (1977) at Fort Saskatchewan. Ethane from the Edmonton ethane plant is not required (except if a shutdown occurs to Cochrane or Empress) and therefore goes directly to storage. The liquid ethane in storage is periodically *batched* down the 30 cm Cochin Pipeline 2900 km to the U.S.A. and Windsor, Ontario. The Cochin Pipeline (1978) alternates ethylene (12-15 000 bbl./d), ethane (40 000 bbl./d) and propane (10-15 000 bbl./d) (in that order) in batch lots down the line. No physical object separates the liquids. Commercial customers remove the liquified gases at points along the pipeline. The interface between the liquids is purified at Windsor, Ontario.

LPG Storage

Ethane, ethylene, propane and propane-plus in liquid form are stored in underground salt caverns near Fort Saskatchewan, Alberta. Dome has two caverns each for ethane, propane and propane-plus. Dow has four caverns for ethylene. These caverns are made possible by the large salt deposits deep under the Fort Saskatchewan area. (The salt deposit (plus other factors) originally attracted the Dow chlor-alkali plant, which in turn attracted the Dow vinyl chloride monomer plant and in turn the Diamond Shamrock-Alberta Gas polyvinyl chloride plant. The salt deposits also made caverns possible, allowing for storage of ethylene for Dow's vinyl chloride monomer and ethylene oxide plants. Fort Saskatchewan is therefore a natural storage and distribution point for batching of ethylene, ethane and propane down the Cochin Pipeline and propane-plus down the Interprovincial Pipeline.



LPG Storage Cavern
Figure P6

The caverns are made by drilling a deep hole into the salt formation and dumping water down to dissolve the salt. When not in use the cavern is filled with a saturated salt solution covered by oil. The oil is necessary to keep the tear drop shape.

The brine and oil are pumped out whenever storage of ethylene or LPG is desired. The brine is stored above ground in a holding pond.

ETHYLENE AND ITS DERIVATIVES
EXTRACTION, DISTRIBUTION, AND STORAGE OF ETHANE

1. The fractionation of crude oil at Sarnia into naphtha for ethylene production also produces large amounts of fuel oil. Explain why the production of these large amounts of fuel oil fits into the Ontario energy market so well.

2. Explain why ethylene in Alberta is produced from ethane extracted from natural gas rather than being produced from naphtha.

3. Draw structural formulas for the eight simplest alkanes. (See Table P2.)

4. Use intermolecular attractions (e.g., London dispersion forces) to explain the relative boiling points of the eight simplest alkanes. (See Table P2.)

5. Besides methane what other gases are left in the residue gas from an LPG plant?

6. The residue from an LPG plant contains 1 to 1.5 percent by mass of ethane (assume 1.5% for this question and the next). If the percent of ethane in the natural gas fed to the Dome plant in Edmonton is 20% by mass, what is the percentage yield of the Dome plant in regard to ethane extraction?

7. If the percent of ethane in natural gas fed to the Alberta Natural Gas plant in Cochrane is 6.0%, what is the percentage yield of the ANG plant in regard to ethane extraction?

8. When not in use underground CPG caverns are filled with a saturated salt solution covered by oil. Why are a saturated salt solution and oil used? Explain.

ETHYLENE AND ITS DERIVATIVES
ETHYLENE

History of Ethylene

Johann Becker, a German, was the first chemist to publish an observation of ethylene in a book (published in 1667). Becker wrote "*There is clear proof that fire is connected with alcohol and oil of vitrol* (sulfuric acid) *when both are properly purified. For as soon as they are mixed they cause fire which in a closed vessel is quenched but when opened inflames again*". Undoubtedly Becker has observed the production and burning of ethylene. By the late 1700's this observation seemed to have become common. Four Dutch chemists (Deimann, Van Troostwyk, Bondt and Louwrenburgh) communicated in 1795 that "*every chemist knows from experience that on distilling ether from a mixture of alcohol* (ethanol) *and concentrated vitriolic acid* (sulfuric acid) *an amount of gas is developed which, towards the end of the operation, increases so much that the glass apparatus easily breaks unless suitably chosen*".

The reaction observed by these early chemists was the dehydration of ethanol, catalyzed by sulfuric acid.

$$C_2H_5OH_{(l)} + \text{heat} \xrightarrow[\text{catalyst}]{H_2SO_4} C_2H_{4(g)} + H_2O_{(l)}$$

The Dutch chemists also produced ethylene (which they called *carbonaceous oily hydrogen gas* or *oily gas*, because of an oily substance produced when ethylene reacted with chlorine) by thermal cracking catalyzed by alumina (aluminum oxide). (Their work with solid catalysts to promote a gaseous reaction was also a first.)

History of the Industrial Preparation of Ethylene

Before and during World War I ethylene was produced from ethanol using high temperatures and either an alumina or phosphoric acid catalyst. The ethylene was used before World War I as an intermediate to produce ethane as a refrigerant. During World War I ethylene was used to produce poisonous mustard gas (2-thio-1,1-dichloroethane).

During World War II ethylene was produced on a large scale by the catalyzed hydrogenation of acetylene. Ethylene was also produced in ovens used to prepare coke for steel production. Hydrogen gas is also produced as part of coke oven gas and was required before World War II to produce ammonia. Ethylene was extracted as a condensation by-product of the hydrogen extraction from the coke oven gas.

The Union Carbide Corporation of U.S.A. piloted the production of ethylene from ethane in the early 1920's and started a strong ethylene industry. The demands for ethylene (especially by the automotive industry) to produce synthetics has grown ever since.

Ethane Cracking

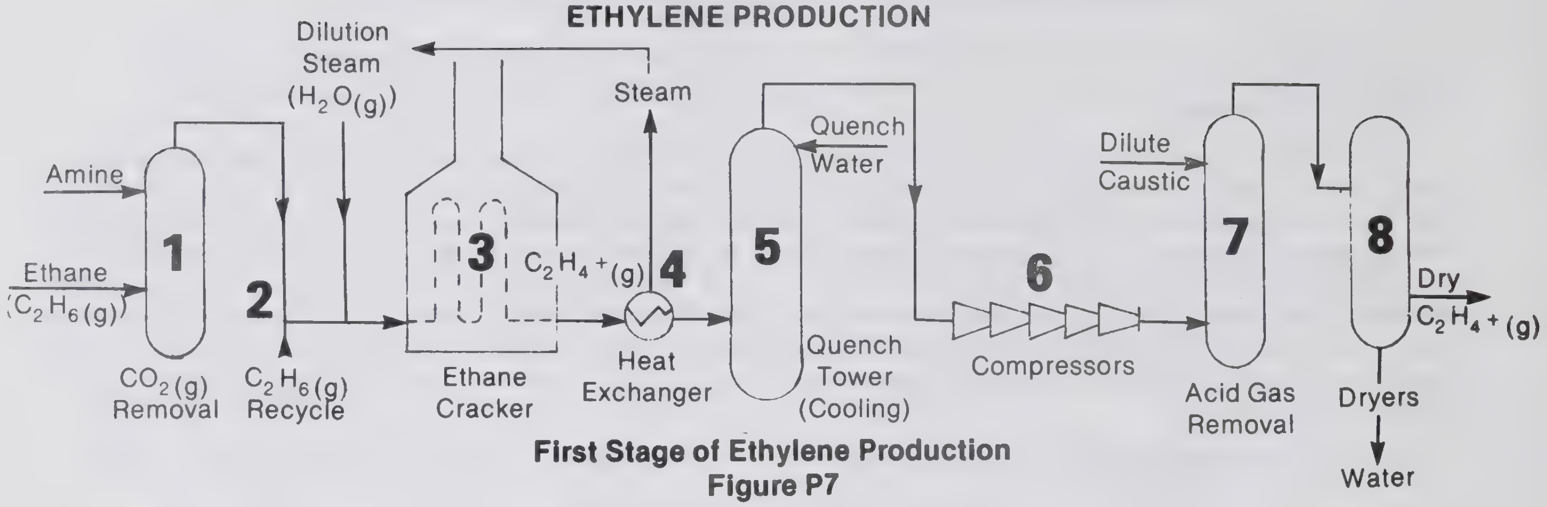
Ethylene is produced on a large scale basis by either ethane "cracking (dehydrogenation)" or naphtha cracking depending on available feedstock and on markets (see earlier discussion).

The AGEC world scale ethylene plant at Joffre (near Red Deer, Alberta) employs ethane cracking. The term *cracking* refers to the breaking down of larger molecules into smaller molecules. In the case of ethane cracking, ethane is converted into ethylene (a smaller molecule).

$$C_2H_{6(g)} + \text{heat} \longrightarrow C_2H_{4(g)} + H_{2(g)}$$

The cracking itself is only a small part of the total process. Because of impurities in the intake gas (i.e., carbon dioxide and hydrogen sulfide) and because of side-reactions which produce small amounts of by-products, a long train of purification vessels follow the ethane cracking vessel.

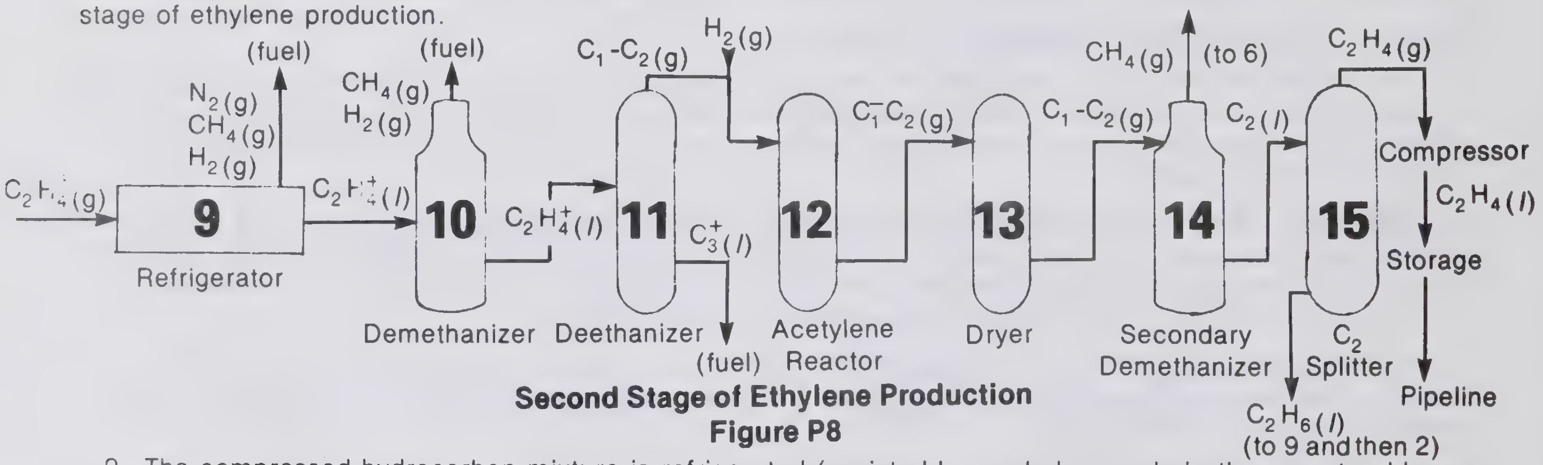
ETHYLENE PRODUCTION



First Stage of Ethylene Production
Figure P7

1. The liquid ethane feed is first gasified and then an amine is used to remove the carbon dioxide. 2. The gaseous ethene is combined with recycled ethane and diluted with hot, pressurized steam before entering the ethane cracker. 3. The ethane cracker operates at about 800 °C and 1 to 2 atmospheres pressure. The fuel for the ethane cracker and other parts of the ethylene plant is primarily supplied by small quantities of by-products (i.e., hydrogen, methane, propane, butane and pentanes-plus) from the plant.

4. The hot mixture of hydrocarbons (60-75 % ethylene) leaving the cracker is used to heat steam used by the cracker. 5. After leaving the heat exchangers the gas is cooled by direct contact with quench water. The cooling is followed by compressors (6), hydrogen sulfide removal (7) and driers (8) in preparation for the second stage of ethylene production.



Second Stage of Ethylene Production
Figure P8

9. The compressed hydrocarbon mixture is refrigerated (assisted by cooled, recycled ethane and cold gas from the demethanizer) to convert the entire mixture, except for methane and hydrogen, into the liquid phase. 10. The liquid phase is fed into the demethanizer where any remaining low boiling methane and hydrogen is distilled off. (The cold, gaseous phase from the refrigerators and the demethanizer are combined, used for cooling in the refrigerator, and are then used as fuel for the plant.)

11. The liquid phase from the demethanizer is fed to the de-ethanizer. The C_1 and C_2 hydrocarbons are distilled from the C_3+ hydrocarbons by an appropriate control of temperature and pressure. The C_3+ liquids can then be separated into propane, butane and C_5+ fractions by distillation (see ethane extraction from natural gas). The C_3+ hydrocarbons, plus methane and hydrogen are only produced in sufficient quantities to supplement the plant's fuel requirements.

12. The gaseous phase from the de-ethanizer contains C_1-C_2 hydrocarbons. The acetylene (C_2H_2) is removed by a reaction with hydrogen to produce ethylene and ethane. The resulting gas is then dried (13) and demethanized again (14) (to remove water and methane produced in the acetylene reactor) before being fed to the C_2 splitter. 15. The C_2 splitter separates the ethylene and ethane by condensing the ethane. (Under standard pressure (101 kPa) ethylene and ethane have boiling points of -104 °C and -89 °C respectively.) The liquid ethane is recycled back through the refrigerator unit (to assist the liquification of products from the ethane cracker) before it is reintroduced as a gas into the ethane cracker.

The ethylene produced by the AGEC ethylene plant is 99.9 % pure. The ethane to ethylene conversion is only about a 60 % yield without ethane recycling and is about a 75 % yield with ethane recycling.

The gaseous ethylene from the C_2 splitter must be condensed and then either stored or pumped directly into a pipeline. At the AGEC plant at Joffre, Alberta storage is very limited. The liquid ethylene is pumped by pipeline to ethylene derivative plants or underground caverns for use in the derivative plants or batch shipping down the Cochin Pipeline from Fort Saskatchewan, Alberta.

ETHYLENE AND ITS DERIVATIVES
PRODUCTION OF ETHYLENE

1. Write an equation using structural formulas for the first method of producing ethylene in the laboratory.

2. Write an equation using structural formulas for the production of ethylene during World War II from acetylene (ethyne) by hydrogenation.

3. Write an equation using structural formulas for the production of ethylene by ethane cracking (dehydrogenation).

4. Use heats of formation to determine the molar heat of reaction for the production of ethylene by the cracking (dehydration) of ethanol (Question 1). (Assume water vapor is produced.)

5. Determine the molar heat of reaction for the hydrogenation of acetylene to produce ethylene (Question 2).

6. Determine the molar heat of reaction for the production of ethylene from ethane (Question 3).

ETHYLENE AND ITS DERIVATIVES
PRODUCTION OF ETHYLENE

7. Use Le Chatelier's Principle to explain the selection of the reaction temperature and pressure in the ethane cracking unit.

8. Write an equation for the production of hydrogen gas (for the acetylene reactor) and carbon dioxide from methane and water vapor over a nickel(II) oxide catalyst. (This same reaction is used to produce hydrogen for hydrogenation of unsaturates in tar sands plants and to produce hydrogen and carbon dioxide for urea and ammonia production in fertilizer plants.)

9. Write equations for one or more possible reactions for the production of acetylene as an undesirable by-product in the ethane cracker.

10. Write an equation using structural formulas for the reaction which occurs in the acetylene reactor.

11. Why must the acetylene be separated from the ethylene by a selective chemical reaction rather than by a physical separation such as fractional distillation?

12. Write equations for one or more possible reactions for the production of methane as an undesireable by-product in the ethane cracker.

13. The acid-gas removal unit and the dryer are necessary to remove $CO_{2(g)}$ and $H_2O_{(g)}$ respectively. Write equations for one or more possible reactions for the production of $CO_{2(g)}$ and/or $H_2O_{(g)}$ as undesireable by-products in the ethane cracker.

ETHYLENE AND ITS DERIVATIVES
POLYETHYLENE

Ethylene Derivatives

Each ethylene derivative studied in this unit will follow a pattern of *history, production,* and *uses*. The ethylene derivatives which will be studied are:

1. polyethylene
2. vinyl chloride
3. polyvinyl chloride
4. ethylene oxide
5. ethylene glycol
6. ethanolamines

History of Polyethylene

Polyethylene was accidently discovered in 1933 by research chemists of Imperial Chemical Industries Ltd. (ICI) at Winnington, England by the English chemists, Fawcett and Gibson, working in the general research area of high pressure reactions. The particular reaction which led to the accidental discovery was that between ethylene and benzaldehyde. The discovery resulted because the desired high pressure reaction did not occur. The benzaldehyde escaped through a leak and the ethylene polymerized to "a waxy solid found in the reaction tube". The significance of the discovery was not immediate as witnessed by the fact that Fawcett and Gibson again tried *the ethylene - benzaldehyde reaction* (ignoring the undesired reaction). Fortunately the benzaldehyde leaked again (from a different place) and a polymer (polyethylene) was again produced. Fawcett and Gibson confirmed that the *undesired* product was a polymer by establishing that the product had a very large molar mass. This was not the first polymer discovered but it was the first polyethylene discovered.

Research on the high-pressure reactions of ethylene had to be curtailed for about two years due to another (nonfruitful) undesired reaction. Ethylene at temperatures of about 170 °C and pressures about 1000 atmospheres tends to explosively decompose into its elements. By December of 1935, ICI had developed the technology necessary to contain (without rupture) the ethylene decompositions. On December 19, 1935 J.G. Paton and E.G. Williams restarted the study of ethylene reactions by making a trial run with the new steel bomb apparatus containing ethylene alone. They waited until after normal working hours in case the explosive decomposition of the ethylene was not contained by the new apparatus. Difficulty was encountered in maintaining the pressure in the reaction vessel and a leak was suspected. However, they compensated by continuing to feed in ethylene until the supply of ethylene in the gas compressor was exhausted. After depressurizing and cooling, Paton and Williams were amazed to find the vessel filled with a white, waxy polymer of ethylene.

An investigation of the properties of polyethylene indicated an immediate widespread application as a waterproof electrical insulator. The insulating properties made polyethylene very important to the production of wire for underground and underwater use and to the scaling down of large Radar units for aircraft use.

ICI brought a commercial polyethylene plant into operation in 1939. Before this first plant was in operation markets had developed such that a larger plant was being designed to start production in 1942. The largest amount of the production of polyethylene during World War II went to Radar and underwater cables. Polyethylene was produced on a small scale in Germany during World War II but was not used to any appreciable extent. The U.S.A. (with technical advise from ICI) built two large plants by 1943 to produce polyethylene for Radar and multichannel underground telephone cables.

In 1953 a German chemist, Karl Ziegler, unexpectedly discovered during his research of organometallic compounds that alkylaluminum compounds combined with titanium tetrachloride catalyzed the polymerization of ethylene. (Ziegler received a Nobel Prize for his work.) The result was that ethylene could be polymerized at or near room temperature and pressure and with the added bonus of higher mass, more linear (less branched) polymers. The more linear character resulted in a higher density, higher melting point stiffer type of polyethylene.

Further research led to the refinement of both the ICI and Ziegler processes to decrease and increase branching respectively.

POLYETHYLENE

Polymerization

Polymerization may be defined as the process of forming very large (high molar mass) molecules from many small molecules. The small starting molecules are called *monomers* (*one part*). The resulting large molecules are called *polymers* (*many parts*). Generally polymerization is classified as being addition polymerization or condensation polymerization. *Condensation polymerization* involves the combining of monomers which result in the loss of simple molecules such as water or hydrogen chloride. (See ALCHEM Unit O, *Foods and Their Analogs.*) *Addition polymerization* can occur with all compounds that contain carbon-carbon double bonds. (The problem is to find the correct catalyst, and temperature and pressure, and to find a use for the polymer produced.)

Polymerization of Ethylene

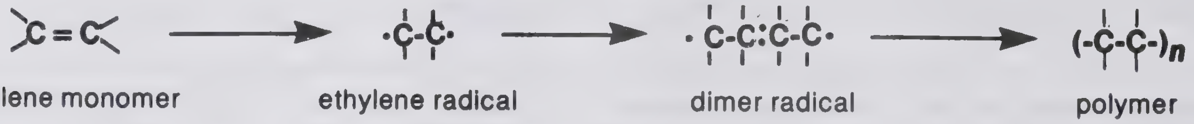
Ethylene undergoes addition polymerization to produce polyethylene.

$$n\ CH_2 = CH_2 \xrightarrow[\text{pressure}]{\text{catalyst, heat,}} \cdots\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\cdots$$

or $(\text{-}CH_2\text{-}CH_2\text{-})_n$

ethylene **polyethylene**

The simplest explanation for the production of polyethylene from ethylene involves the formation of intermediate free radicals. (Free radicals are species with single (unpaired) nonbonded electrons.)



The ethylene radicals are formed by the breaking of one of the bonds of the carbon-carbon double bond. The radical is very reactive and will react with another radical to produce a dimer radical. These radicals continue to react with one another until a very large polymer (about 700 to 10 000 ethane units long) is produced.

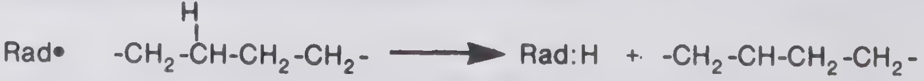
Actually the reaction indicated above would be very difficult to initiate or sustain. Catalysts (initiators) are introduced to speed and control the polymerization. Most of the catalysts up to 1953 were of the free radical type.

$$\text{Catalyst} \longrightarrow \text{Rad}\bullet + e^-$$

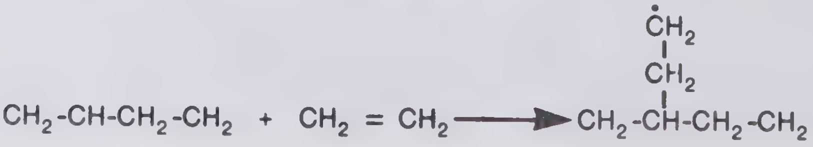
$$\text{Rad}\bullet + CH_2 = CH_2 \longrightarrow \text{Rad}CH_2\text{-}CH_2\bullet$$

$$\text{Rad}CH_2\text{-}CH_2\bullet + CH_2 = CH_2 \longrightarrow \text{Rad}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\bullet$$

Unfortunately side branches (rather than linear chains) may develop which result in poor packing of the polymer chains. The poor packing yields a low density, low melting point, soft ("squeeze bottle") type of polyethylene. The branching is due to the reaction of a catalyst radical with a hydrogen on the chain to produce a new radical with an unpaired electron in the middle of the chain.



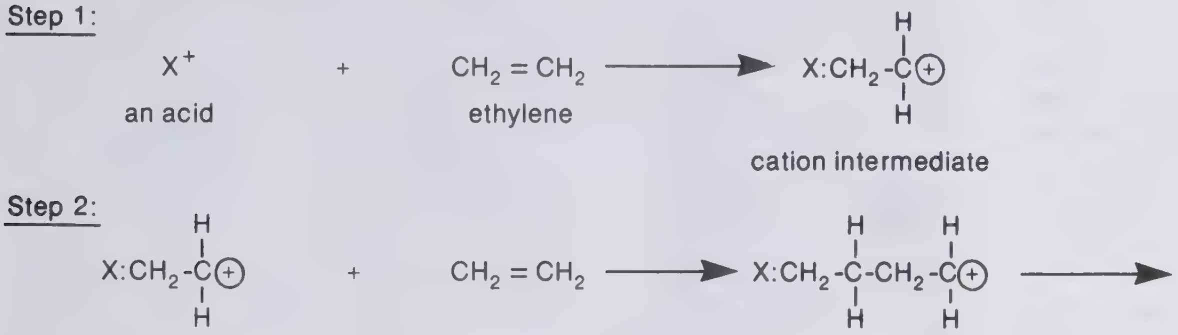
$$\text{Rad}\bullet\quad \text{-}CH_2\text{-}\overset{\overset{\displaystyle H}{|}}{C}H\text{-}CH_2\text{-}CH_2\text{-} \longrightarrow \text{Rad:H} + \text{-}CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}$$



$$CH_2\text{-}CH\text{-}CH_2\text{-}CH_2 + CH_2 = CH_2 \longrightarrow CH_2\text{-}\overset{\overset{\overset{\displaystyle \dot{C}H_2}{|}}{CH_2}}{\underset{|}{}}\!\!\!\!\!CH\text{-}CH_2\text{-}CH_2$$

Ionic Polymerization of Ethylene

Until 1953 free radical polymerization was the main commercial method of producing any addition polymer. (the one exception was the acid-catalyzed (cationic) polymerization used to produce butyl rubber which is explained later in this unit.) Since the 1953 discovery by Karl Ziegler (at the Max Planck Institute for Coal Research in Germany) of the ionic polymerization of ethylene, the whole field of ionic polymerization has overshadowed that of free radical polymerization. Generally the catalyst used acts as either an acid (to produce an intermediate cation) or as a base (to produce an intermediate anion). (An acid in this case (i.e., a Lewis acid) is defined as something which can accept a pair of electrons (i.e., like a H^+ ion can)).



The reactions can be visualized as that of both electrons (from one of the two bonds between the carbon atoms in ethylene) being transferred to form a bond between the cation intermediate and ethylene.

Polyethylene can be produced by ionic polymerization under much milder conditions than with free radical polymerization and branching does not occur as readily. The resulting polyethylene is denser, stronger and has a higher melting point.

History of Polyethylene in Alberta

A 9 Gg/a (9 million kilogram per year) polyethylene plant (Canada's first) was built in Edmonton in 1952-53 by Canadian Industries Ltd. (CIL). CIL is a subsidiary of the original polyethylene producer, Imperial Chemical Industries of Great Britain (ICI). The plant was expanded in 1959 to triple production (to 32 Gg/a (32 million kilograms per year)). In 1970 and 1971 CIL added facilities to process the raw polyethylene pellets into polyethylene film and to use the film to produce bags, wrappings and vapor barriers.

CIL and Dupont originally had plans for 135-180 Gg/a (135-180 million kilograms per year) low density and high density polyethylene plants (respectively) in Alberta. The CIL plant was to be near Edmonton and the Dupont plant near Red Deer. Both companies backed out declaring a lack of adequate markets for the polyethylene. Dupont has recently doubled the output of their Sarnia high density polyethylene plant to 205 Gg/a (205 million kilograms per year). Union Carbide has built a 180 Gg/a (180 million kilograms per year) low density polyethylene plant, also at Sarnia.

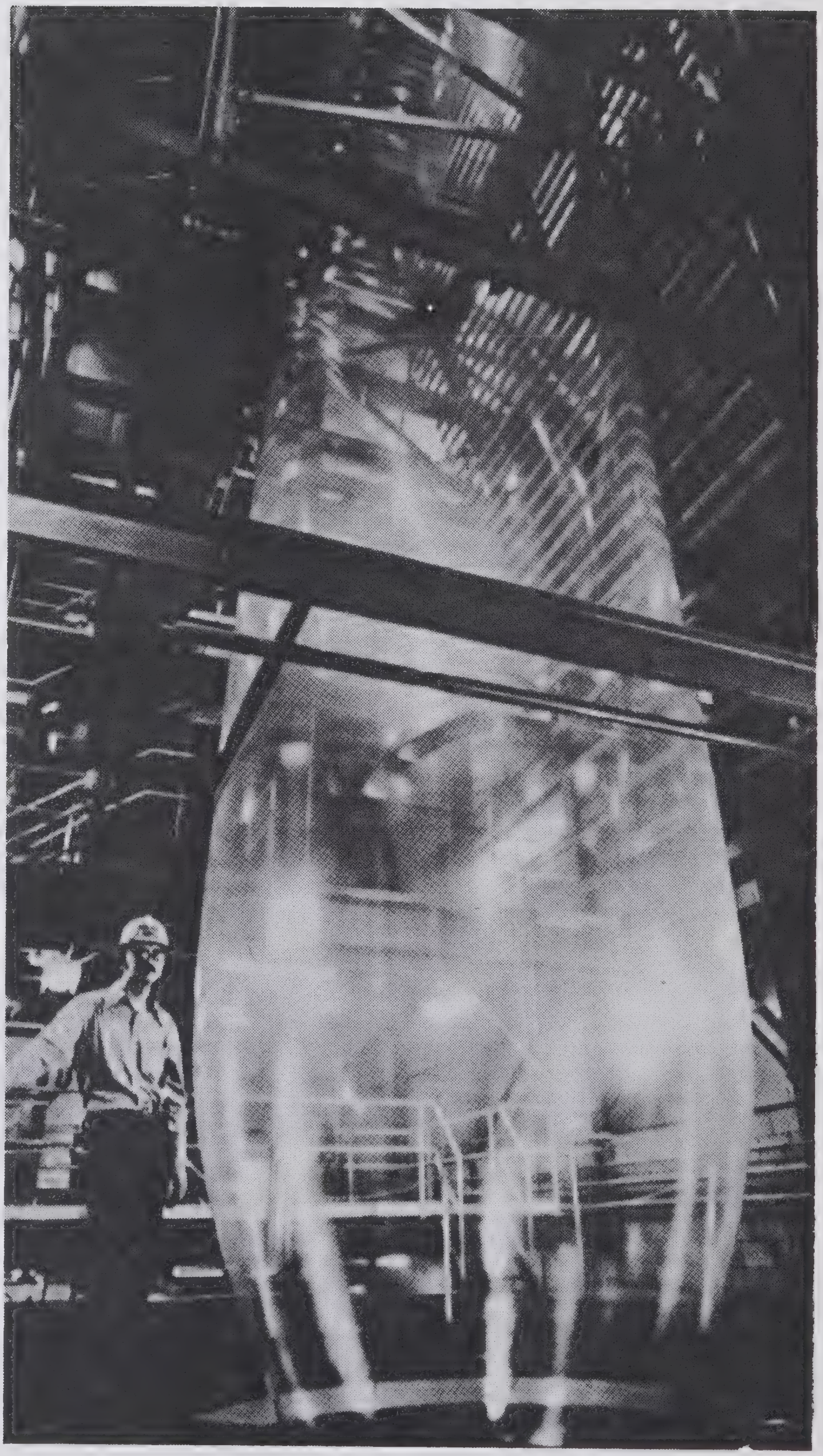
CIL's Edmonton Polyethylene Plant

CIL's Edmonton polyethylene plant is a fully integrated plant. CIL removes ethane from natural gas, produces ethylene by ethane cracking and use the low to medium density polyethylene that they produce to make consumer products. However, all of this is on a relatively small scale (i.e., world scale ethylene and polyethylene plants are 10 to 15 times larger than the CIL plant in Edmonton).

The CIL plant was Canada's first polyethylene plant. The plant was located in Edmonton because of the availability of an ethane rich natural gas feed northwest of Edmonton. The ethane extraction and ethylene production are similar to the methods described previously.

ETHYLENE AND ITS DERIVATIVES
POLYETHYLENE

The reactors at the Edmonton CIL plant are not unlike 30 cm long gun barrels. The ethylene is fed into the reactors at pressures of about 170 MPa (17 hundred atmospheres) using peroxide catalysts. A syrup-like polymer is obtained from the reactor. The unreacted ethylene is recycled. After the polymer is cooled and the pressure is reduced, the polymer is transferred to a hopper. The polyethylene is squeezed out of the bottom of the hopper in hundreds of 3 mm in diameter spaghetti-like strings. Whirling knife blades chop the polyethylene strings into 3 mm pellets. Some pellets are impregnated with carbon to produce a black pellet (resin) (for polyethylene pipe and cable covering) or other additives may be used to produce specialty resins. The pellets (called resins) may be shipped in 25 kg bags, 1000 kg cardboard containers or 65 t (65 thousand kilogram) hopper rail cars, or the pellets may be further processed at the CIL plant. Since 1970 CIL in Edmonton has added facilities to produce polyethylene film (up to 12 m wide and 0.4 mm thick). The film is produced as a bubble (the largest film producing bubble in Canada). CIL now converts the film into various bags, food wrapping and rolls of construction film.



Big Bubble

ETHYLENE AND ITS DERIVATIVES
VINYL CHLORIDE

1. Write an equation for the high pressure decomposition of ethylene into its elements.

2. Determine the molar heat of reaction for the decomposition of ethylene.

3. What makes the ethylene decomposition reaction explosive?

4. Explain the difference in molecular structure between low density and high density polyethylene and in how they are respectively produced.

5. Explain why high density polyethylene has a higher melting point and is harder than low density polyethylene.

6. Write equations to represent the reaction of ethylene with a radical and with a Ziegler catalyst in the first step of the formation of polyethylene.

ETHYLENE AND ITS DERIVATIVES
VINYL CHLORIDE

Vinyl Chloride

Vinyl chloride, a gas, is the monomer used by produce polyvinyl chloride (PVC). The history and production of vinyl chloride is followed by the section on PVC.

Vinyl Chloride (History and Process)

H.V. Regnault (the first to prepare carbon tetrachloride) was in 1835 the first chemist to prepare vinyl chloride (a gas with a boiling point of -13 °C, also called VC, VCM (vinyl chloride monomer) or chloroethane). The method he used was never considered economical for large scale commercial vinyl chloride plants.

1. Regnault first reacted ethylene with chlorine to get a liquid. (This reaction was first done by the Dutch chemists who discovered ethylene.) Write an equation using structural formulas for this addition reaction.

2. Regnault then reacted the ethylene dichloride (1,2-dichloroethane) produced in the first step with potassium hydroxide to produce vinyl chloride, potassium chloride and water. Write an equation using structural formulas for the organic compounds.

Eight years later F. Klatte and his co-workers in Germany discovered that vinyl chloride may be produced from acetylene and hydrogen chloride. This process was used in the first commercial vinyl chloride plants. Acetylene (ethyne) had to be produced first.

3. The first step in the production of acetylene was the reaction of lime (calcium oxide) with coke (assume pure carbon) to produce calcium carbide (CaC_2) and carbon monoxide. Write a balanced chemical equation for this step.

4. The second step in the acetylene production was the reaction of calcium carbide with water to produce calcium hydroxide and acetylene. Write a balanced equation for this step.

5. Vinyl chloride can then be produced by reacting acetylene with hydrogen chloride using mercury(II) chloride on coke to catalyze the reaction. Write a balanced equation using structural formulas.

6. The above process, although old, is still used. This process using acetylene is not used at the Alberta vinyl chloride plant. Why might this process be important (especially in Alberta) at some time in the future? (See the Dow chlor-alkali process described in the ALCHEM 30 core unit, *Electrochemistry.*)

7. Acetylene can also be produced by pyrolysis (extreme heating) of natural gas (assume methane). The reaction mechanism involved is not known. Propose a reaction or set of reactions which might be involved in the production of acetylene from natural gas. (By-product and/or intermediates may be produced also.)

ETHYLENE AND ITS DERIVATIVES
VINYL CHLORIDE

The majority of vinyl chloride is presently produced from ethylene. Three different methods of producing vinyl chloride from ethylene are described below.

8. The simplest way of producing vinyl chloride from ethylene is a single step substitution reaction of ethylene with chlorine. Write a balanced chemical equation using structural formulas.

9. What problem must be dealt with following the above reaction?

10. Undesirable by-products may be avoided if a two step method is used as described below. The first step involves the reaction between ethylene, hydrogen chloride and oxygen (from the air) to produce ethylene dichloride (1,2-dichloroethane, DCE) and water. Write a balanced equation using structural formulas for the organic compounds.

11. In the second step the DCE is cracked (dehydrochlorinated) to produce vinyl chloride and hydrogen chloride. Write a balanced equation using structural formulas.

12. Cancel common compounds and add the above two equations to get a net molecular equation.

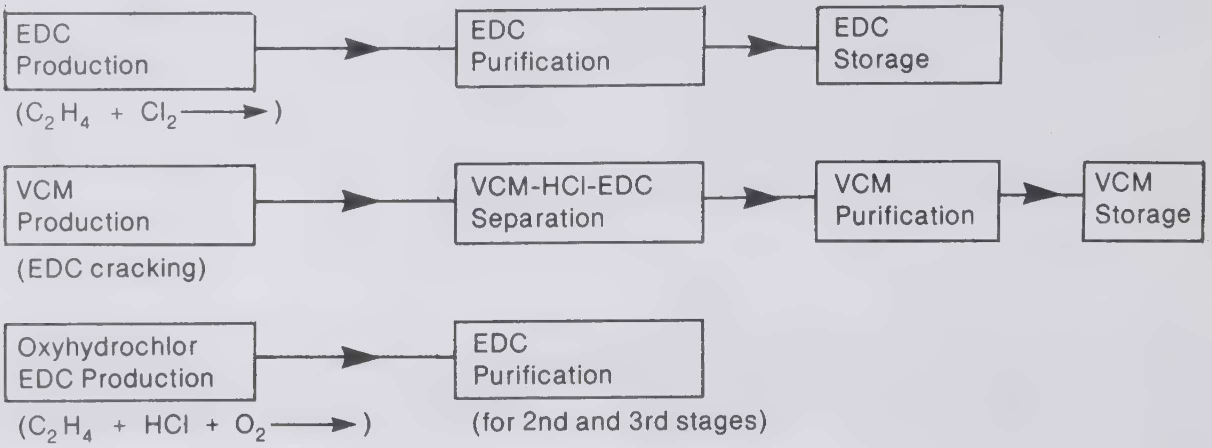
13. What advantage does this two step method have over the one method described previously?

If a cheap source of chlorine is available a third method is used. This method is used in the Dow Chemical vinyl chloride plant at Fort Saskatchewan. Dow has had a chlor-alkali plant at Fort Saskatchewan for many years but had to expand when the vinyl chloride plant was built.

14. The vinyl chloride process used by Dow combines the two step process previously described with the addition of chlorine to ethylene. Rewrite the three equations (this time in molecular form). Cancel common compounds and add the three equations to get a net molecular equation.

15. In terms of raw material why use the three step process for the production of VCM?

16. The three reactions employed in Dow's plant at Fort Saskatchewan are represented by the partial plant flowchart below. Complete the flowchart by using lines and arrows to show the input of raw materials and the movement of intermediate materials between the three reaction streams.



Note: The remainder of the questions require knowledge of heats of formation.

17. Determine the molar heat of reaction of ethylene in the substitution reaction of ethylene with chlorine.

18. Determine the molar heat of reaction for the production of vinyl chloride by the two step method. (Assume $H_2O_{(g)}$ is produced.)

19. Determine the molar heat of reaction for the production of vinyl chloride by the three step method. (Assume $H_2O_{(g)}$ is produced.)

History and Development of Polyvinyl Chloride (PVC)

F. Klatte, the German chemist, and his co-workers who first produced vinyl chloride later discovered the catalyzing effect of peroxides on the polymerization of vinyl chloride. At the same time work was being done on the polymerization of vinyl chloride by light (first observed by Regnault, the discover of vinyl chloride). Nearly a hundred years passed after the discovery of vinyl chloride before the problems of producing and using PVC were solved sufficiently to start commercial production.

The production of PVC escalated rapidly. Until 1965 PVC was the synthetic polymer produced in greatest quantity. PVC had a head start on polyethylene by five to ten years, but polyethylene surpassed PVC in 1965 in terms of quantity produced.

Polyvinyl chloride is produced in Canada by Esso Chemical at Sarnia, Ontario, B.F. Goodrich at Niagara Falls, Ontario and Shwinigan, Quebec, Monsanto at LaSalle, Quebec, and Diamond Shamrock-Alberta Gas At Fort Saskatchewan, Alberta. The Fort Saskatchewan PVC plant (1979) produces 100 Gg/a (100 million kilograms per year) of polymer and may be expanded to 180 Gg/a as market conditions dictate.

Production of PVC

The production of PVC is an addition (free-radical) polymerization of the monomer vinyl chloride. The polymerization reaction is highly exothermic. The heat generated must be dissipated or else a low molar mass, relatively valueless polymer is produced. As a result *bulk* PVC production (similar to polyethylene production) is not feasible. The PVC must be produced in a medium with high heat capacity and conductance in order to dissipate the heat. The medium (usually an aqueous solution or suspension) must also suspend the PVC so that small droplets of PVC are produced (rather than a large precipitating mass which would affect the operation of the heat exhangers). The particles of PVC may be either filtered or centrifuged from the suspension. The removal of the PVC from the reactor is continuous but controlled. It has been empirically determined that the rate of polymerization is most rapid when the reaction is about 70 percent complete. As a result a build up of polymer in suspension is allowed before extraction is started.

The use of peroxides as free radical initiators (catalysts) for the polymerization of vinyl chloride has been known since the turn of the century. Research after 1953 on Ziegler-Natta (ionic) catalysts for PVC production has not been fruitful. Free radical catalysts remain as the catalysts for PVC production.

Effects of VCM

The PVC reactors (containing residual VCM) must occasionally be cleaned. This turns out to be an extremely hazardous job. Vinyl chloride (not PVC) has been blamed for the deaths of at least 45 petrochemical workers around the world. Because the effects of the vinyl chloride take up to fifteen years to show up, initial work with vinyl chloride was generally done without safety precautions. In fact, initially plastic workers sniffed vinyl chloride gas to get high (a cheap drunk). Unfortunately vinyl chloride is carcinogenic (cancer producing). After a long period a sudden rapid growth of malignant cells in the victim's liver leads to death within months.

Newer PVC reactors (such as those in the PVC plant at Fort Saskatchewan) are cleaned by mechanical means. Men do not have to crawl into the PVC reactors anymore. The hygiene branch of the Alberta Department of Labor has set an exposure standard of five parts per million. The Alberta standard is believed to have a built in 10 fold safety margin. (The standard in Great Britain is 25, in the United States is 1, and in Ontario is 10 parts per million.) No death has been attributed to vinyl chloride in VCM plants or in any of the thousands of businesses where finished PVC products are turned out.

Vinyl chloride *emissions* from vinyl chloride and polyvinyl chloride plants are also a concern. Environment Canada published new regulations in 1978 under the Clean Air Act to significantly reduce vinyl chloride gas emissions. The new regulations reduced the total VC emissions for four VC plants from 5000 t/a to 250 t/a.

Uses of Polyvinyl Chloride

PVC can be made flexible or rigid, foamed, used as a coating, made into sheets or films, extruded, or molded (by blow, injection or compression). The consumption of PVC generally follows the percentages given below.

Building and Construction: 40%

Moldings, flooring, lighting, panels and siding, pipe and conduit, pipe fittings, rainwater systems, soffits, fascias, swimming pool liners, weatherstripping, window frames and profiles.

Home Furnishings: 19%

Appliances, furniture, wall coverings and wood surface films, housewares.

Electrical: 7.4%

Wire and cable coating.

Packaging: 6.4%

Bottles, liners and gaskets, coatings, film sheet.

Recreation: 6.2%

Phonograph records, toys, sporting goods.

Transportation: 5.1%

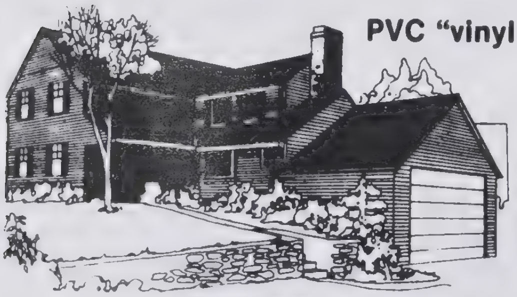
Auto mats, tops, upholstery and seat covers.

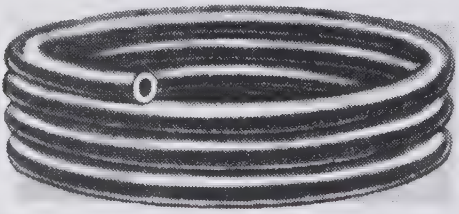
Apparel: 4.4%

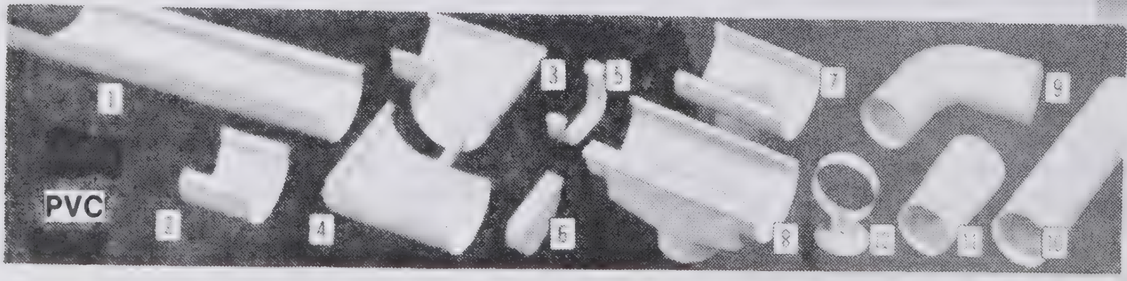
Footware, outerwear, specialties.

Miscellaneous: 11.5%

Medical: tubing, solution bags, heart/lung machine components, surgical implants; credit cards, tools.







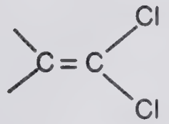
ETHYLENE AND ITS DERIVATIVES
POLYVINYL CHLORIDE

1. What is meant by the statement that the rate of polymerization of VCM has been *empirically* determined?

2. Propose a free radical reaction mechanism for the production of PVC (similar to the mechanism presented earlier for polyethylene).

Write structural formulas for the polymers formed from the following monomers. (Show three monomer units in the structural formula of the polymer.)

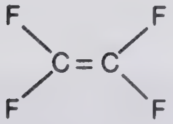
3.



vinylidene chloride
(1,1-dichloroethene)

Saran

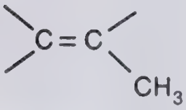
4.



perfluoroethylene
(tetrafluoroethene)

Teflon

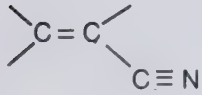
5.



propylene
(propene)

polypropylene

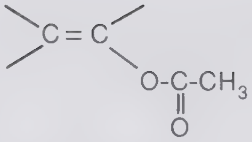
6.



acrylonitrile
(vinyl cyanide)

Acrilan, Orlon

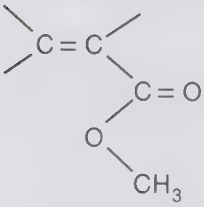
7.



vinyl acetate

polyvinyl acetate (PVA)
Vinylite

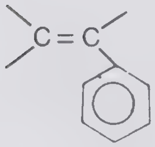
8.



methyl methacrylate

Lucite, Plexiglass
(acrylics)

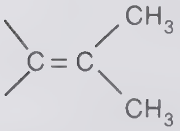
9.



styrene
(vinyl benzene)
(phenylethene)

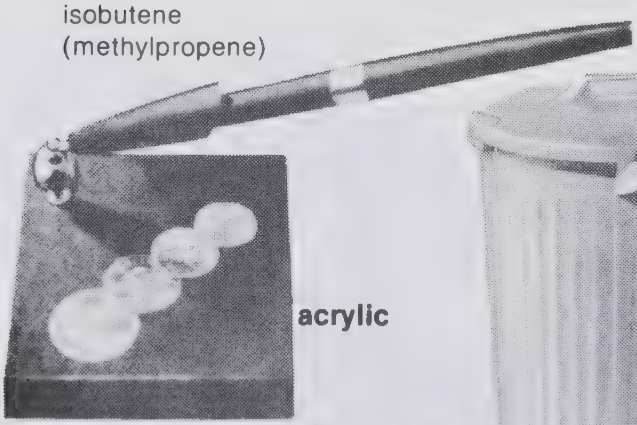
polystyrene, polyvinyl benzene
styrofoam, Styron

10.

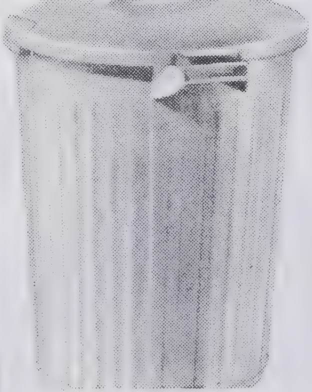


isobutene
(methylpropene)

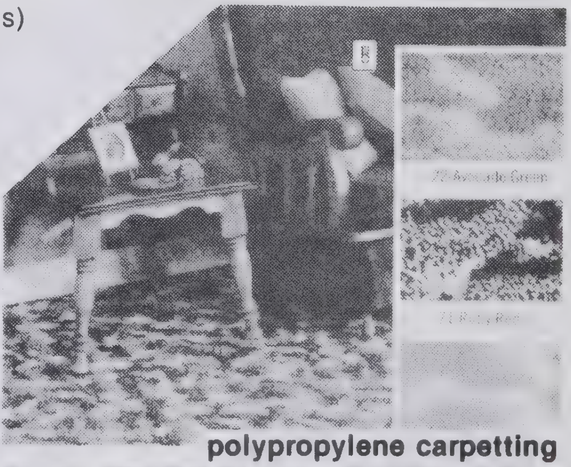
Butyl rubber
(inner tubes)



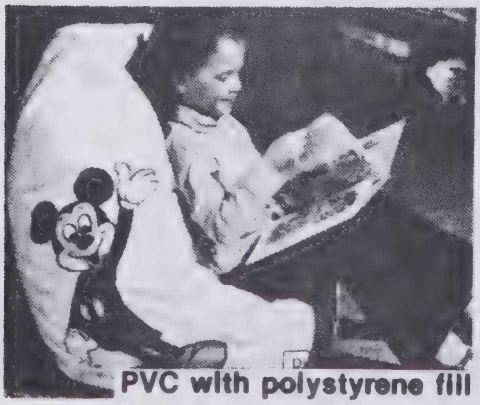
acrylic



polyethylene

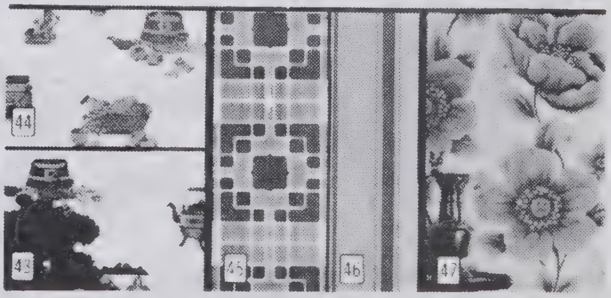


polypropylene carpetting



PVC with polystyrene fill

Teflon coated frypan



vinyl coated wallpaper

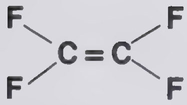
ETHYLENE AND ITS DERIVATIVES
IDENTIFICATION OF SOME POLYMERS — LAB P1

Purpose:

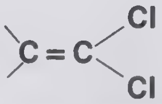
1. To see and work with a variety of common polymers.
2. To become familiar with a technique for identifying polymers.
3. To identify unknown polymers from a list of eleven possibles.

Prelab Information:

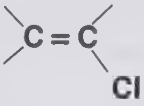
The monomers for the polymers studied in this lab are listed below. One or two trade names are provided for each polymer. Each polymer is made by many companies under a different trade name. (See the *CRC Handbook.*)



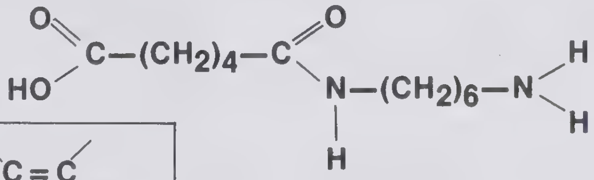
polytetrafluoroethene
monomer
(Teflon)



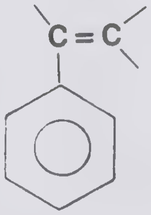
polyvinylidene
chloride
monomer
(Saran)



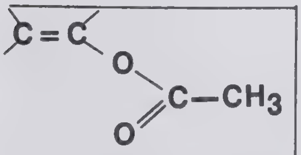
polyvinyl chloride
monomer
(Corvic)



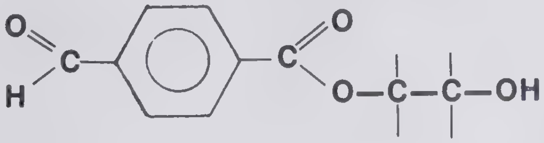
nylon 6-6
monomer
(Zytel 101)



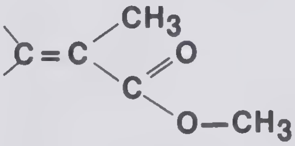
polystyrene
monomer
(Styron, Styrofoam)



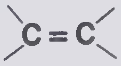
polyvinyl acetate
monomer
(Vinylite)



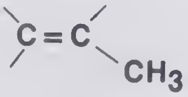
a polyester
monomer
(Dacron, Mylar)



an acrylic
monomer
(Lucite, Plexiglass)



polyethylene
monomer
(Ethafoam, Dur-X)



polypropylene
monomer
(AviSun)

Prelab Exercise:

Use the flowchart in the Procedure to identify the following polymers.

Polymer	Burns in Flame (✓)	Continues to Burn (✓)	Flame Color	Odor	I.D.
A	—	—	—	HCl	
B	✓	—	blue; yellow tip	burning hair	
C	✓	✓	yellow (soot)	vinegar	
D	✓	✓	blue; yellow tip	fruit	

Materials:

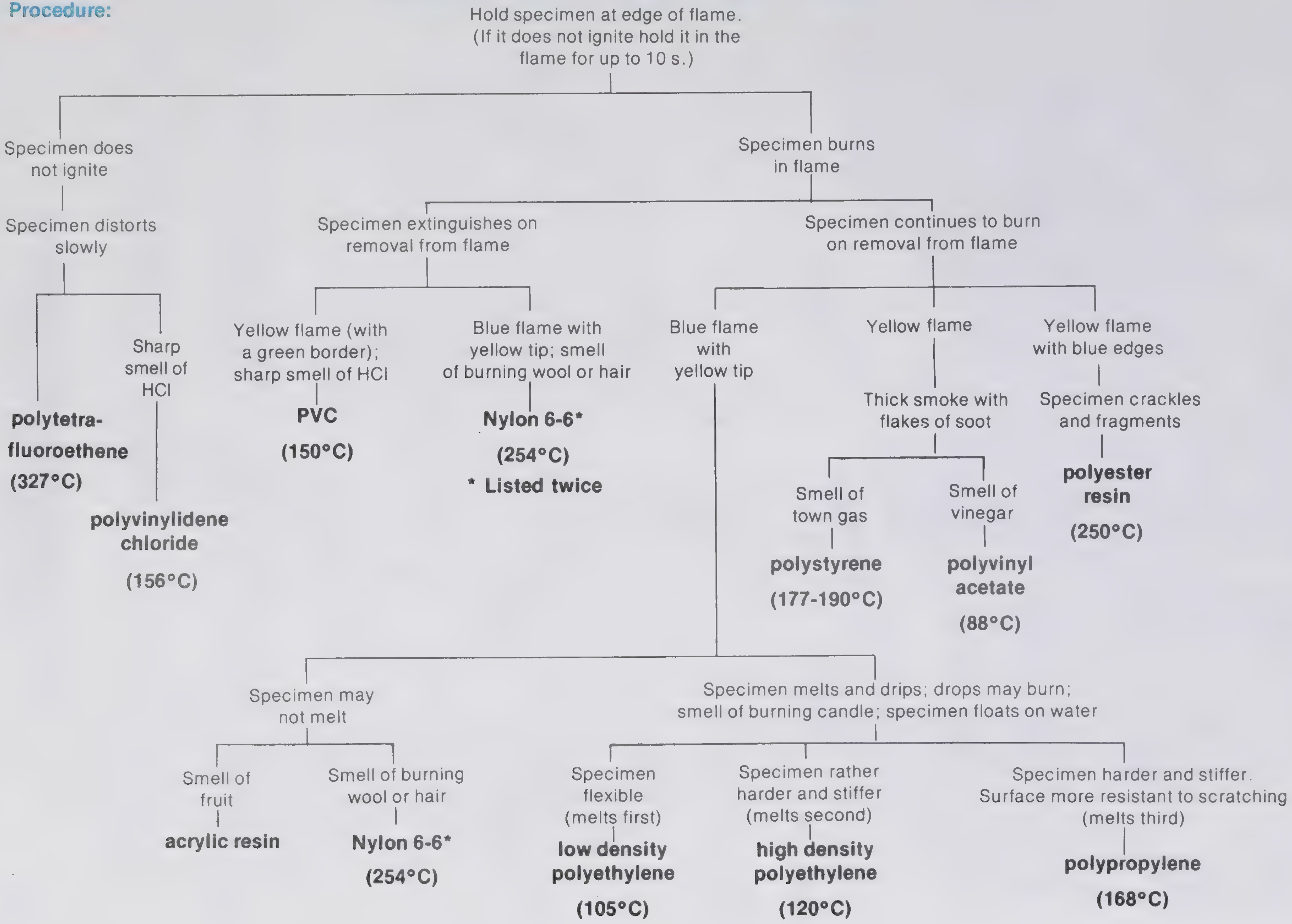
1 - scoopula
1 - tweezer
1 - bunsen burner
1 - striker
2 - paper towels
- steel wool

polytetrafluoroethene
polyvinylidene chloride
polyvinyl chloride (PVC)
nylon 6-6
polystyrene
polyvinyl acetate (PVA)

polyester resin
acrylic resin
polyethylene (LDP)
polyethylene (HDP)
polypropylene

ETHYLENE AND ITS DERIVATIVES
IDENTIFICATION OF SOME POLYMERS — LAB P1

Procedure:


Hold specimen at edge of flame.
(If it does not ignite hold it in the flame for up to 10 s.)
Specimen does not ignite
Specimen distorts slowly
polytetrafluoroethene
(327°C)
Sharp smell of HCl
polyvinylidene chloride
(156°C)
Specimen burns in flame
Specimen extinguishes on removal from flame
Yellow flame (with a green border); sharp smell of HCl
PVC
(150°C)
Blue flame with yellow tip; smell of burning wool or hair
Nylon 6-6*
(254°C)
* Listed twice
Specimen continues to burn on removal from flame
Blue flame with yellow tip
Yellow flame
Thick smoke with flakes of soot
Smell of town gas
polystyrene
(177-190°C)
Smell of vinegar
polyvinyl acetate
(88°C)
Yellow flame with blue edges
Specimen crackles and fragments
polyester resin
(250°C)
Specimen may not melt
Smell of fruit
acrylic resin
Smell of burning wool or hair
Nylon 6-6*
(254°C)
Specimen melts and drips; drops may burn; smell of burning candle; specimen floats on water
Specimen flexible (melts first)
low density polyethylene
(105°C)
Specimen rather harder and stiffer (melts second)
high density polyethylene
(120°C)
Specimen harder and stiffer. Surface more resistant to scratching (melts third)
polypropylene
(168°C)

ETHYLENE AND ITS DERIVATIVES
IDENTIFICATION OF SOME POLYMERS — LAB P1

Procedure:

Notes:

Touching pellets with the hand might transfer salt to the pellet which in turn will produce a yellow flame. The samples need not be done in any particular order. Pick up all or, if crowded, only a couple samples before starting the tests.

1. Obtain one pellet of each of the polymers by the procedure outlined by the teacher; i.e.,
   a. obtain a paper towel and write the numbers 1-10 spaced on it.
   b. use a tweezer to obtain one pellet of each of the numbered polymers and place them on the paper towel beside their respective numbers.
2. Light the bunsen burner. Obtain a noiseless blue flame with an inner cone.
3. Use the tweezers to place an unknown pellet on the scoopula. Hold the pellet on the edge of the flame for up to 10 s.
4. Use the Identification of Polymers flowchart in the Procedure to identify the polymer. Record all observations in the table provided.

Note:

There are no two unknowns the same in this lab. Repeat the tests if two numbers are identified as the same polymer. The Teflon and PVC polymers and the polyethylene and polypropylene polymers are difficult to distinguish. In these cases narrow the identification down to an either/or answer.

5. Discard the burned or melted residue on a paper towel and use steel wool to clean the scoopula.
6. Proceed with the next polymer by following the flowchart.

Observations:

Caution: Waft odors towards the nose by hand. Do not smell directly.

Polymer	Burns in Flame (✓)	Continues to Burn (✓)	Flame Color	Odor	I.D.	Polymer	Burns in Flame ( )	Continues to Burn ( )	Flame Color	Odor	I.D.
1						6					
2						7					
3						8					
4						9					
5						10					

Questions:

1. What further test(s) could be done to distinguish between LDP and HDP?

List the types of intermolecular bonding in the following polymers. Use structural formulas for illustration.

2. polypropylene
3. PVC
4. Nylon 6-6

5. Butyl rubber is an addition polymer of methylpropene which is especially impervious to gases and as a result is used for inner tubes. Write a structural equation to represent the polymerization to form butyl rubber.

ETHYLENE AND ITS DERIVATIVES
ETHYLENE OXIDE — ETHYLENE GLYCOL

History of Ethylene Oxide and Ethylene Glycol

Note:

The uses of ethylene oxide and ethylene glycol will be presented in a section following the history. Ethylene glycol (1,2-ethanediol) was prepared first by the German chemist C.A. Wurtz in 1856. The synthesis was a four step process. (Write the balanced equations using structural formulas for the organic compounds in each reaction described below.)

1. First ethylene was prepared by the dehydration of ethanol using an acid catalyst. (Recall that this reaction resulted in the accidental discovery of ethylene.)

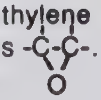
2. In the second step the ethylene was reacted with bromine to produce 1,2-dibromoethane (ethylene dibromide).

3. Wurtz then reacted the 1,2-dibromoethane with anhydrous sodium acetate to produce the 1,2-diacetate of ethane and sodium bromide.

4. The diacetate was then hydrolyzed (reacted with water) using an acid catalyst to produce ethylene glycol and acetic (ethanoic) acid.

Three years later in 1859 Wurtz was able to produce ethylene oxide from ethylene glycol by a two step method. (The production of ethylene oxide from ethylene glycol is the reverse of what is done now.)

5. Wurtz reacted ethylene glycol with hydrogen chloride to produce ethylene chlorohydrin (2-chloroethanol).

6. The ethylene chlorohydrin was then reacted with potassium hydroxide to produce ethylene oxide (1,2-epoxyethane), water and potassium chloride. (The structural formula for ethylene oxide is .)

7. The lengthy process of producing ethylene oxide from ethylene that was used by Wurtz (see Questions 1 to 6 above) was shortened four years later (in 1863) to two steps by L. Carius. Carius discovered the addition reaction of ethylene with hypochlorous acid to produce ethylene chlorohydrin. (This reaction was then followed by the reaction in the previous question.)

8. Wurtz went on to study the reactions of the extremely reactive gas, ethylene oxide. Among the many reactions which Wurtz researched was the production of ethylene glycol by the hydrolysis of ethylene oxide. (This addition reaction is similar to the addition reaction between cyclopropane and chlorine.)

Industrial History of Ethylene Oxide and Derivatives

The commercial production of ethylene oxide and its derivatives was influenced by two major markets - mustard gas for World War I and ethylene glycol for automobile antifreeze. Mustard gas (a gas that produced sickness but few deaths) was either produced from ethylene chlorohydrin (from Question 7) or directly from ethylene. (Write balanced chemical equations, using structural formulas for the organic compounds, for the following reactions.)

9. The Germans in 1917 used a two step method (after producing ethylene chlorohydrin from ethylene and hypochlorous acid) to generate mustard gas. First ethylene chlorohydrin was reacted with sodium sulfide to produce sodium chloride and thiodiglycol $(CH_2OHCH_2)_2S$.

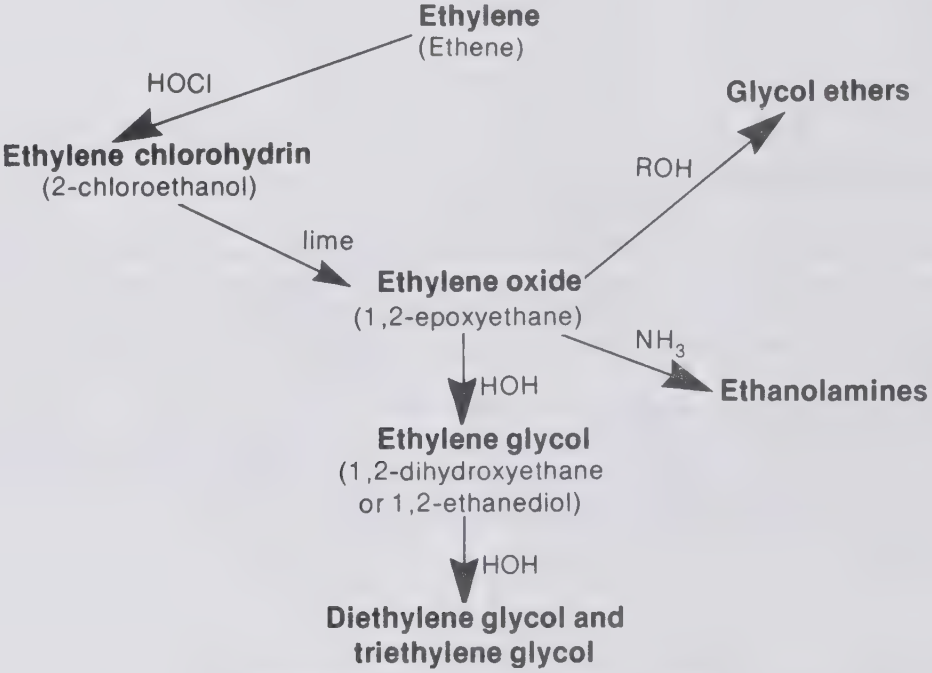
10. Then the thiodiglycol was reacted with concentrated hydrochloric acid to produce mustard gas, $(CH_2ClCH_2)_2S$.

11. The Allies preferred a direct synthesis of mustard gas from ethylene. Ethylene was reacted with disulfur dichloride to produce mustard gas and sulfur. (For simplicity in the equation assume the formula for sulfur is S.)

12. The first large scale ethylene glycol plants in the 1920's produced ethylene glycol by the hydrolysis of ethylene chlorohydrin (the reverse of the reaction carried out by Wurtz (see Question 5)). (What undesireable by-product was produced?)

The process was shortly changed to one in which ethylene oxide is a recoverable intermediate. As a result, the production of ethylene glycol from ethylene chlorohydrin took two steps rather than one. The advantage was that the recoverable intermediate, ethylene oxide, could be used to produce end products other than ethylene glycol. *The method of producing the ethylene oxide has changed since then, but ethylene oxide is still produced today as an important intermediate.*

The flowchart below illustrates the petrochemical processes associated with ethylene oxide in the period 1925-1930. Use the flowchart to assist in writing chemical equations for the reactions which follow. Write structural formulas for the organic compounds in the equations.



Ethylene Oxide from 1925 to 1930
Figure P9

13. Ethylene reacts with hypochlorous acid to produce ethylene chlorohydrin.

14. Ethylene chlorohydrin reacts with slaked lime ($Ca(OH)_2$) to produce ethylene oxide and by-products. (Are there any common uses for the by-products?)

15. Ethylene oxide is hydrolyzed using an acid catalyst to produce ethylene glycol. (The acid catalyst effect was discovered by A. Bigot in 1891.)

16. Two molecules of ethylene glycol (monoethylene glycol, MEG) react in the presence of an acid catalyst to produce a molecule of diethylene glycol (DEG, $CH_2OHCH_2OCH_2CH_2OH$) and a molecule of water.

17. A molecule of DEG reacts with a molecule of MEG in the presence of an acid catalyst to produce triethylene glycol (TEG). (The presence of DEG and TEG with the MEG was first detected by A.V. Lourenco in 1863, three years after Wurtz had first produced MEG from ethylene oxide.)

Ethylene oxide may also be used to produce ethanolamines. (An *amine* is a compound derived from ammonia (NH_3) by substituting an organic group for a hydrogen to produce RNH_2, R_2NH or R_3N. *Ethanolamines* are amines produced by substituting ethanol ($-CH_2CH_2OH$) groups for the hydrogens in ammonia.)

18. Ethylene oxide reacts with ammonia to produce monoethanolamine (2-hydroxyethylamine, $H_2NCH_2CH_2OH$).

19. Monoethanolamine (MEA) reacts with ethylene oxide to produce diethanolamine (DEA).

20. DEA reacts with ethylene oxide to produce triethanolamine (TEA).

Ethylene oxide may also be used to produce glycol ethers (CH_2OHCH_2OR). (An ether is an organic compound represented by $R\text{-}O\text{-}R^1$.)

21. Ethylene oxide reacts with methanol in the presence of an acid catalyst to produce 2-methoxyethanol ($CH_2OHCH_2OCH_3$).

22. Ethylene oxide reacts with ethanol to produce 2-ethoxyethanol.

Production of Ethylene Oxide by Direct Oxidation

Of all the reactions included in the ethylene oxide flowchart in the previous section, the one reaction which has changed the most over time is the preparation of ethylene oxide. Recall that Wurtz produced ethylene oxide from ethylene in 1859 by a six step process and that Carius in 1863 reduced the process to two steps with ethylene chlorohydrin as an intermediate.

Wurtz reported in 1863 that he had been unsuccessful in his many attempts to react ethylene with oxygen to produce ethylene oxide. Others were also unsuccessful until 1931 when S. Lenher of the U.S.A. and T.E. Lefort of France independently developed processes for the oxidation of ethylene to ethylene oxide. The Lefort process gained the greatest acceptance. Lefort used a silver catalyst with moderate temperatures and pressures.

The modifications on the Lefort process have been minor. All direct oxidation ethylene oxide plants operate with very similar chemistry. The differences between the processes used at different plants lie in the balancing of variables to get a more economical process. A balance must be struck between maximizing yield and safety and minimizing costs. To obtain a maximum theoretical yield from the process is possible but it is also very costly. The cost would be such that the selling price of the ethylene oxide would not be competitive.

An indication of the difficulty of achieving an optimum balance of cost and yield is that no one patented oxidation process has received widespread acceptance throughout the world. However, oxidation processes in total have completely taken over from the chlorohydrin process for ethylene oxide production.

Direct oxidation processes for the production of ethylene oxide may be classified into two types - air and oxygen. *Air processes* feed air or air enriched with oxygen into the oxidation vessel. *Oxygen processes* feed 85 percent or better oxygen into the reaction vessel. Regardless of the process (either air or oxygen) used, the chemistry is the same. Very few by-products are formed in either oxidation process. Carbon dioxide and water are the only substantive by-products. Methanal (formaldehyde) and ethanal (acetaldehyde) are formed in very small amounts.

Note:

When writing the chemical equations below use structural formulas for the organic compounds.

1. Write the balanced chemical equation for the reaction of ethylene (ethene) with oxygen to produce ethylene oxide (1,2-epoxyethane). (The ratio of ethylene used to oxygen used is about 1:2. This is the only desired reaction. The other reactions that follow produce undesireable by-products.)

2. Write a balanced chemical equation for the oxygen combustion of ethylene. (As the temperature rises this combustion reaction becomes more of a problem.)

3. Write a balanced chemical equation for the oxygen combustion of ethylene oxide. (Isotopic labelling has shown that about 20 percent of the carbon dioxide by-product produced in the direct oxidation process is from ethylene oxide.)

4. Write a balanced chemical equation for the reaction of ethylene with oxygen to produce methanal (formaldehyde, HCHO).

5. Write a balanced chemical equation for the reaction of ethylene with oxygen to produce ethanal (acetaldehyde, CH_3CHO). (The reaction in Question 6, rather than this reaction, is believed to be the major producer of ethanal.)

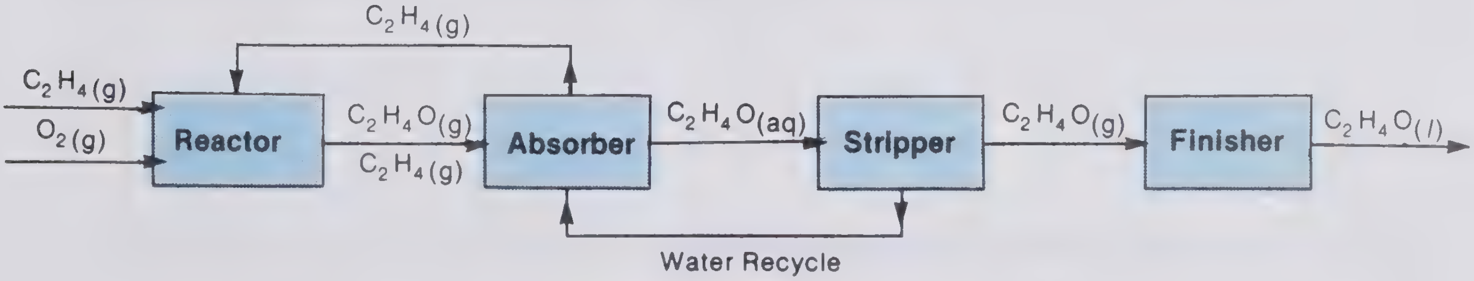
6. Write a balanced chemical equation for the decomposition of ethylene oxide to produce ethanal (acetaldehyde, CH_3CHO).

7. Determine the molar heat of reaction for the desired reaction between ethylene and oxygen to produce ethylene oxide.

8. How might the heat of reaction of ethylene to ethylene oxide interfere with the production of pure ethylene oxide?

Ethylene Oxide - Ethylene Glycol Plants

The Dow ethylene oxide plant (1978) at Fort Saskatchewan, Alberta employs the oxygen-feed process for the direct oxidation of ethylene to ethylene oxide. The plant consumes 135 Gg/a (135 million kilograms per year) of ethylene. (The boiling point of ethylene oxide is 13 °C.)



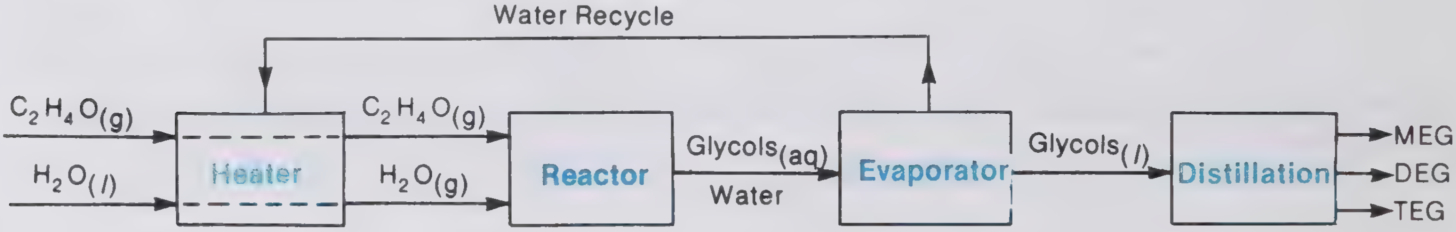
Ethylene Oxide Plant
Figure P10

ETHYLENE AND ITS DERIVATIVES
ETHYLENE OXIDE — ETHYLENE GLYCOL

1. If 100 percent of the 135 Gg/a of ethylene is converted over a catalyst into ethylene oxide, what mass of ethylene oxide is produced each year?

2. In the *absorber* unit the ethylene oxide is absorbed (dissolved) in water, while the rest of the gas stream is recycled or sent through further reactor and absorber units. Explain why ethylene oxide dissolves more readily in water than the other gases from the reactor.

The Dow ethylene glycols plant (1978) at Fort Saskatchewan converts their ethylene oxide into ethylene glycols by the following process. The production of ethylene glycol from ethylene oxide is known for its simplicity (in contrast to ethylene oxide production).



Ethylene Glycol Plant
Figure P11

Note:

See the previous historical treatment for the reactions involved.

3. If the molar heat of reaction of ethylene oxide and water to produce ethylene glycol is -161.9 kJ/mol then why are the ethylene oxide and water heated before reaction?

4. What catalyst is generally used for hydrolysis reactions?

5. Explain why water has a lower boiling point than the ethylene glycols.

6. Predict the relative boiling points of the ethylene glycols and explain.

7. If the Fort Saskatchewan ethylene glycol plant is to produce about 450 kg/d of MEG (monoethylene glycol), what mass of ethylene oxide is consumed per day to produce MEG? (Assume 100% conversion.)

Table P3
Effect of Ethylene Oxide: Water Ratio on Glycol Distribution

Initial C_2H_4O:H_2O Molar Ratio	Hydration Products, % of Total Oxide			
	Ethylene Glycol (MEG)	Diethylene Glycol (DEG)	Triethylene Glycol (TEG)	Higher Polyglycol
1:10.5	82.3	12.7	—	—
1:7.9	77.5	17.5	—	—
1:4.2	65.7	27.0	2.3	—
1:2.1	47.2	34.5	13.0	0.3
1:0.61	15.7	26.0	19.8	33.5

(From *Ethylene and its Industrial Derivatives*, edited by S.A. Miller, Ernest Benn Limited, London, 1969, p.591.)

Note: See the previous historical treatment for the reactions involved.

8. Explain why increasing the amount of water in an ethylene oxide to ethylene glycol reactor decreases the amounts of DEG, TEG and higher ethylene glycols produced.

9. Explain why increasing the amount of water increases the cost of production.

10. What factors ultimately determines the ratio of C_2H_4O:H_2O used in a plant?

Uses of Ethylene Oxide

The major use of ethylene oxide is as an intermediate to produce ethylene glycols, ethanolamines and glycol ethers (the reactions, for which, were given earlier). Other minor uses of ethylene oxide are:

1. *sterilization.* (Ethylene oxide mixed with 8 to 10 times its mass of carbon dioxide may be used at low temperatures to eliminate bacteria and spores.)

2. *fumigant.* (Ethylene oxide treatment aids in the preservation of foodstuffs and may be used to eliminate certain undesired insects.)

3. *anti-acid.* (Ethylene oxide may be used to neutralize a system where conventional alkali anti-acids may be undesireable.)

4. *rocket or jet fuel.* (Ethylene oxide under proper conditions undergoes an exothermic auto-decomposition forming propulsive gases. It is also claimed that ethylene oxide blended with nitromethane (dragster fuel) improves various characteristics of the fuel.)

Uses of Ethylene Glycol (MEG)

1. The major use of ethylene glycol is as an antifreeze compound. During the early years of the automobile various solutes were added to water in the cooling system to avoid freezing. (When water in the cooling system freezes, it expands and may crack the engine block.) Initially various salts and then alcohols (i.e., methanol) were used to depress the freezing point. Eventually MEG became the major antifreeze compound. The addition of MEG lowers the freezing point and eliminates cracked blocks. Not only is MEG used as an antifreeze in automobile cooling systems but it is also used in lead storage (car) batteries (in special circumstances) and in dynamite. Dynamite contains nitroglycerine (1,2,3-trinitropropane) absorbed in a porous material. Unfortunately when the dynamite would freeze detonation would not occur. Lack of caution when thawing the dynamite resulted in many fatal accidents. The solution turned out to be the addition of nitroglycol (1,2-dinitroethane) to the dynamite. The nitroglycol additive eliminated freezing and (as a bonus) was also explosive. The low freezing point dynamite was prepared by adding the MEG to the glycerine in order that both could be nitrated together.

2. The second major use of ethylene glycol (in North America) is in the production of polyesters marketed commercially as Dacron (Du Pont), Fortrel (Beaunit Mills), Kodel (Eastman Kodak), Terylene (ICI), Vycron (Celanese) and others. The polyester is essentially the same in each case although the production process may be slightly different. The polyester is a co-polymer (i.e., is produced from two different monomers) of ethylene glycol and terephthalic acid ($HOOCC_6H_4COOH$).

3. Ethylene glycol is also used to produce other polyester resins called glyptals or alkyds. This group of polyesters can not be turned into fibres (like the above mentioned polyesters). As a result these alkyds are used as surface coatings such as lacquers (e.g., alkyd paint).

4. Both oil and water based hydraulic fluids used in such things as automobile brake systems and front enc loaders to transfer power from one point to another contain ethylene glycol. More-modern hydraulic fluids are noncorrosive to rubber and are noninflammable. Ethylene glycol is used in oil based hydraulic fluids to prevent corrosion of rubber components. Nonflammable hydraulic fluids are water based and include ethylene glycol as an important anti-corrosion component.

5. Another use of ethylene glycol is as a *plasticizer* to make polymers softer and more flexible. Cellophane (another form of rayon, both of which are made of cellulose) tends to become very brittle when air dried. The addition of ethylene glycol prevents this brittleness in Cellophane.

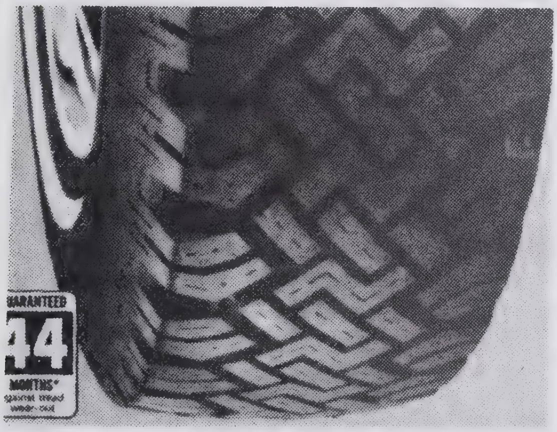
6. Ethylene glycol is used to produce glyoxal (OHCCHO) which was initially used to stop shrinking of rayon fabric. The use of glyoxal has now been extended as an anti-shrink and *permanent-press* additive to polyester fabrics (which, themselves, were made from ethylene glycol).

7. Electrolytic capacitors (i.e., for radios and televisions) commonly employ ethylene glycol to form a boric acid salt paste to separate aluminum foil layers in the capacitor.

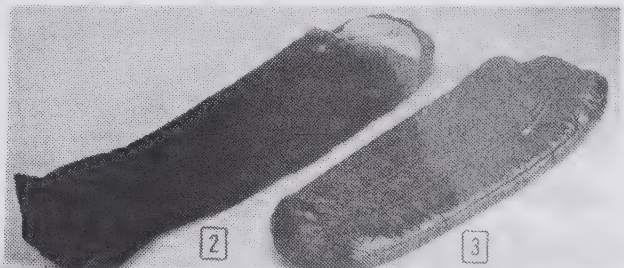
The above list of the uses of ethylene glycol (MEG) is by no means complete. Ethylene glycol is an extremely versatile chemical with current *major* uses extending from very old uses to very new uses.

Uses of Polyethylene Glycols

Polyethylene glycols (e.g., DEG and TEG) are produced as by-products of the production of ethylene glycol. Their uses very much parallel the uses of MEG. One important different application in Alberta is the use of both DEG and TEG as dehydrating agents for well-head natural gas. If water is not removed from the natural gas near the well head, the water reacts with the lower hydrocarbons to produce solid hydrates which could plug the gas pipeline. The water from the gas is absorbed in the polyglycols in the first unit and then the water is stripped from the polyglycol by distillation in a second unit. Since TEG has a lower vapor pressure (evaporates less readily), it is preferred over DEG. (The absorption of water from natural gas by polyethylene glycols is very similar to the absorption of hydrogen sulfide gas from natural gas by ethanolamines (see next page).)

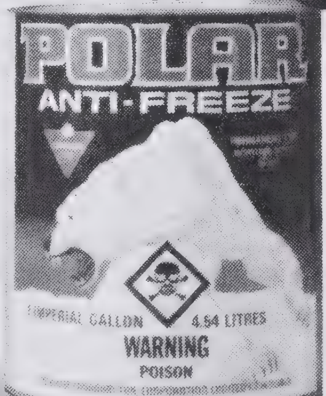


polyester tire



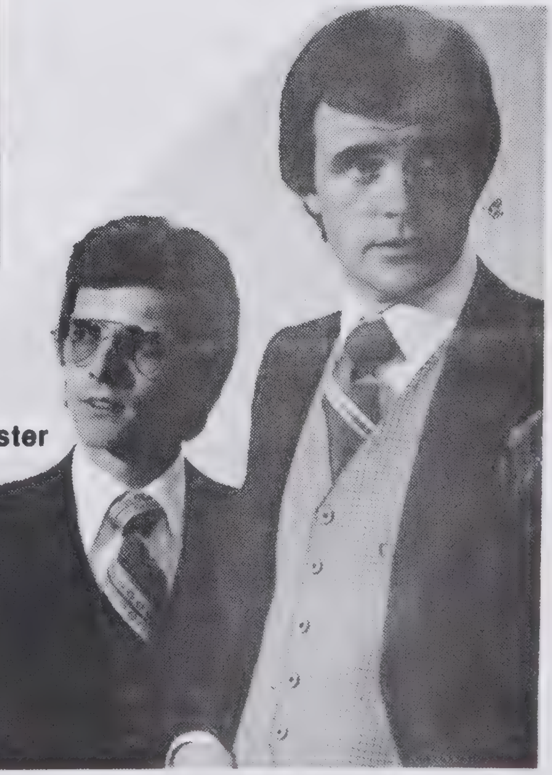
polyester filled

ethylene glycol



alkyd paint

polyester



ETHYLENE AND ITS DERIVATIVES
USES OF ETHYLENE OXIDE AND ETHYLENE GLYCOLS

The first six questions involve the removal of water vapor and hydrogen sulfide gas from natural gas.

1. Ethylene oxide may be reacted with ammonia to produce ethanolamines (e.g., MEA, monoethanolamine, $H_2NCH_2CH_2OH$). Write a balanced equation (using structural formulas) for the reaction to produce MEA.

2. Hydrogen sulfide may be removed from natural gas by passing the sour natural gas stream through aqueous MEA ($H_2NCH_2CH_2OH_{(aq)}$). The reaction involves a proton transfer from the H_2S to the MEA to form $HS^-_{(aq)}$ and $H_3\overset{+}{N}CH_2CH_2OH_{(aq)}$. Write a balanced chemical equation (using structural formulas) for this reaction.

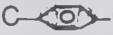
3. The hydrogen sulfide and monoethanolamine may be regenerated by removing the aqeuous solution from the first unit and distilling it in a second unit. The reaction in Question 2 is reversed. Write a balanced chemical equation (using molecular formulas and state of matter) for this reaction.

4. Why are DEA and TEA (di and triethanolamine) better chemicals than MEA for use in hydrogen sulfide extraction units? Explain.

5. Why are DEG and TEG better chemicals than MEG for use in units built to extract water from natural gas? Explain.

6. Why is DEG more commonly used for dehydration of natural gas, even though TEG is chemically preferred?

Questions 7 through 12 relate to the production of the polyesters - Dacron, Fortrel, Terylene, etc.

7. The polyester common to clothing is produced by first reacting two molecules of ethylene glycol with every one molecule of terephthalic acid (1,4-benzenedicarboxylic acid, HOOC——COOH) to produce the diester ($HOCH_2CH_2OOCC_6H_4COOCH_2CH_2OH$). Write a balanced chemical equation (using structural formulas) for this reaction.

8. The reaction in Question 7 can proceed without a catalyst by elevating the temperature. The reaction also proceeds better if the water that is produced is removed. Give two or three reasons why the water should be removed.

9. Ethylene oxide may be reacted with terephthalic (1,4-benzenedicarboxylic acid) to produce the same diester as in Question 7. Write a balanced chemical equation (using structural formulas) for the reaction.

10. Why is the production of the diester from ethylene oxide superior to the production of the diester from ethylene glycol?

11. The polyester produced by the polymerization of the diester in Questions 7 and 9 may be represented by dropping a $HOCH_2CH_2O$- group from one end of the diester molecule and a -H from the other end. Draw a structural formula to represent the polymer. Write some of the trade names for the polyester beside the structural formula.

12. What by-product is produced by the production of the polyester in Question 11?

Ethylene glycol can depress the freezing point of water down to a minimum of -48 °C if a 56 % by volume solution is used. After 56 % the freezing point of the water in the solution begins to rise again until there is 100 % ethylene glycol (which itself will then freeze at -13 °C).

Table P4
Freezing Points of Water in Ethylene Glycol

MEG % by Volume	0	10	20	30	40	50	56	80	90	100
Freezing Point (°C)	0	-4	-9	-17	-28	-38	-48	-45	-28	-13

If an antifreeze is not used in the cooling system of an engine cold weather can result in the water freezing. The ice formed occupies a larger volume and may during expansion cause the engine block to crack. Running an engine containing frozen water will cause overheating and further engine damage. Even *complete* freezing of any ethylene glycol-water solution will not crack the engine block. The water freezes in small crystals (initially suspended in the aqueous ethylene glycol) rather than as a solid block of ice. However, overheating may occur with any sufficiently large cluster of ice crystals which may clog the cooling system.

13. The water in a 38 % by volume ethylene glycol solution will not freeze until -25 °C. If the temperature drops to -30 °C, the water in the solution will not all freeze (regardless of how long the temperature stays at -30 °C). Explain.

14. Explain the sequence of events as MEG antifreeze *good for* 30 °C is subjected to a long term temperature of -55 °C.

15. Why were salts and then alcohols replaced as antifreeze components?

16. Propose an exothermic auto-decomposition reaction for ethylene oxide being used as a rocket or jet fuel.

17. Calculate the molar heat of reaction for the production of ethylene glycol from ethylene oxide. (Assume the use of $H_2O_{(g)}$.)

ETHYLENE AND ITS DERIVATIVES
FURTHER ETHYLENE DERIVATIVES

Optional

As an independent, self-study, library project, prepare a report on an e
unit. The possible further derivatives (not current in Alberta) are:

1. Ethanol and its derivatives (e.g., DDT)
2. Ethyl chloride and its derivatives (e.g., tetraethyl lead)
3. Benzene - ethyl benzene styrene
4. Polystyrene and latex
5. Polyesters from ethylene glycol
6. BS rubber
7. Acrylonitrile and derivatives
8. Vinyl acetate - polyvinyl acetate
9. Acetaldehyde - acetic acid - cellulose acetate
10. Acetaldehyde -, butanol - plasticizers
11. Acetaldehyde - ethylhexanol - plasticizers
12. Ethanolamines - detergents
13. Glycol ethers
14. Ethylene - propylene rubber
15. Polyglycols - urethane foam
16. Methyl chloroform
17. Chlorinated solvents from ethylene dichloride
18. Lucite (Plexiglass)
19. Saran
20. Teflon

Outline

History

1. History of the discovery and laboratory preparation of the derivative from other chemicals and from ethylene.

2. History of the industrial process in the world and in Canada.

Industrial Preparation

A description (and flowchart) of the chemical process for the commercial preparation of the derivative including as much chemistry as possible. Provide as much Canadian information as possible.

Uses of the Derivatives

A list of uses with a short discussion of each use including as much chemistry as possible. Provide chemical equations and formulas wherever possible. Provide as much Canadian information as possible.

Note:

The next revision of this unit will include a polymerization lab and a section on polyvinyl acetate.

6. Two Place Logs

No. Log	No. Log	No. Log	No. Log	No. Log
1.0 .00	3.0 .48	5.0 .70	7.0 .85	9.0 .95
1.1 .04	3.1 .49	5.1 .71	7.1 .85	9.1 .96
1.2 .08	3.2 .51	5.2 .72	7.2 .86	9.2 .96
1.3 .11	3.3 .52	5.3 .72	7.3 .86	9.3 .97
1.4 .15	3.4 .53	5.4 .73	7.4 .87	9.4 .97
1.5 .18	3.5 .54	5.5 .74	7.5 .88	9.5 .98
1.6 .20	3.6 .56	5.6 .75	7.6 .88	9.6 .98
1.7 .23	3.7 .57	5.7 .76	7.7 .89	9.7 .99
1.8 .26	3.8 .58	5.8 .76	7.8 .89	9.8 .99
1.9 .28	3.9 .59	5.9 .77	7.9 .90	9.9 1.00
2.0 .30	4.0 .60	6.0 .78	8.0 .90	1.00 .00
2.1 .32	4.1 .61	6.1 .79	8.1 .91	1.01 .00
2.2 .34	4.2 .62	6.2 .79	8.2 .91	1.02 .01
2.3 .36	4.3 .63	6.3 .80	8.3 .92	1.03 .01
2.4 .38	4.4 .64	6.4 .81	8.4 .92	1.04 .02
2.5 .40	4.5 .65	6.5 .81	8.5 .93	1.05 .02
2.6 .41	4.6 .66	6.6 .82	8.6 .93	1.06 .03
2.7 .43	4.7 .67	6.7 .83	8.7 .94	1.07 .03
2.8 .45	4.8 .68	6.8 .83	8.8 .94	1.08 .03
2.9 .46	4.9 .69	6.9 .84	8.9 .95	1.09 .04

Canada metric Canada métrique

7. Solubilities

t = 25°C P = 101 kPa

$HCl_{(aq)}$	*38%	12.4 mol/L
$H_3PO_{4(aq)}$	85%	14.7 mol/L
$HNO_{3(aq)}$	69%	15.4 mol/L
$CH_3COOH_{(aq)}$	99.5%	17.4 mol/L
$H_2SO_{4(aq)}$	94%	17.6 mol/L
$NH_{3(aq)}$	28%	14.8 mol/L
$NaOH_{(aq)}$	50%	19.1 mol/L
$AgCl_{(aq)}$		4.1×10^{-6} mol/L
$CaCO_{3(aq)}$		6.9×10^{-5} mol/L
$Ca(OH)_{2(aq)}$		6.9×10^{-3} mol/L
$C_{12}H_{22}O_{11(aq)}$		3.8 mol/L
$NaCl_{(aq)}$		5.3 mol/L

* percent by mass

ALCHEM Chemistry

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8. Acid-Base Indicators at 25°C

Indicator	pH Range	$HIn_{(aq)}$	$In^-_{(aq)}$
methyl orange	3.1—4.4	red	yellow
methyl red	4.2—6.3	red	yellow
litmus	6.5—7.5	red	blue
bromthymol blue	6.0—7.6	yellow	blue
phenolphthalein	8.0—9.6	colorless	red
alizarin yellow	10.1—12.0	colorless	violet

9. Relative Strengths of Acids and Bases

	Name of Acid Species	Percent Reaction of 0.10 mol/L Solution	Reaction of 0.10 mol/L Aqueous Acid Species with $H_2O_{(\ell)}$	Name of Base Species	
1 Strong Acids	perchloric acid	100	$HClO_{4(aq)} + H_2O_{(\ell)} \xrightarrow{6} H_3O^+_{(aq)} + ClO^-_{4(aq)}$	perchlorate ion	2
	hydroiodic acid	100	$HI_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + I^-_{(aq)}$	iodide ion	
	hydrobromic acid	100	$HBr_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + Br^-_{(aq)}$	bromide ion	
	hydrochloric acid	100	$HCl_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$	chloride ion	
	nitric acid	100	$HNO_{3(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$	nitrate ion	
	sulfuric acid	100	$H_2SO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + HSO^-_{4(aq)}$	hydrogen sulfate ion	
3	hydronium ion	100	$H_3O^+_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + H_2O_{(\ell)}$	water	Decreasing Strength of Bases
Decreasing Strength of Acids	oxalic acid	53	$HOOCCOOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + HOOCCOO^-_{(aq)}$	hydrogen oxalate ion	
	sulfurous acid ($SO_{2(aq)} + H_2O_{(\ell)}$)	32	$H_2SO_{3(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + HSO^-_{3(aq)}$	hydrogen sulfite ion	
	hydrogen sulfate ion	29	$HSO^-_{4(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + SO^{2-}_{4(aq)}$	sulfate ion	
	methyl orange[7]	—	$HMo_{(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + Mo^-_{(aq)}$	methyl orange ion	
	phosphoric acid	24	$H_3PO_{4(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + H_2PO^-_{4(aq)}$	dihydrogen phosphate ion	
	hydrofluoric acid	8.2	$HF_{(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + F^-_{(aq)}$	fluoride ion	
	nitrous acid	7.3	$HNO_{2(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + NO^-_{2(aq)}$	nitrite ion	5
	bromthymol blue[7]	—	$HBb_{(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + Bb^-_{(aq)}$	bromthymol blue ion	
	benzoic acid	2.6	$C_6H_5COOH_{(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + C_6H_5COO^-_{(aq)}$	benzoate ion	
	hydrogen oxalate ion	2.3	$HOOCCOO^-_{(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + OOCCOO^{2-}_{(aq)}$	oxalate ion	
	ethanoic (acetic) acid	1.3	$CH_3COOH_{(aq)} + H_2O_{(\ell)} \leftrightharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$	acetate ion	
	carbonic acid ($CO_{2(aq)} + H_2O_{(\ell)}$)	0.21	$H_2CO_{3(aq)} + H_2O_{(\ell)} \xleftarrow{6} H_3O^+_{(aq)} + HCO^-_{3(aq)}$	hydrogen carbonate ion	
	phenolphthalein[7]	—	$HPh_{(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + Ph^-_{(aq)}$	phenolphthalein ion	
	hydrogen sulfide	9.8×10^{-2}	$H_2S_{(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + HS^-_{(aq)}$	hydrogen sulfide ion	
5	dihydrogen phosphate ion	7.9×10^{-2}	$H_2PO^-_{4(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + HPO^{2-}_{4(aq)}$	hydrogen phosphate ion	
	hydrogen sulfite ion	4.4×10^{-2}	$HSO^-_{3(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + SO^{2-}_{3(aq)}$	sulfite ion	
	ammonium ion	7.5×10^{-3}	$NH^+_{4(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + NH_{3(aq)}$	ammonia	
	hydrogen carbonate ion	2.4×10^{-3}	$HCO^-_{3(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + CO^{2-}_{3(aq)}$	carbonate ion	Strong Bases
	hydrogen phosphate ion	4.7×10^{-4}	$HPO^{2-}_{4(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + PO^{3-}_{4(aq)}$	phosphate ion	
	hydrogen sulfide ion	3.3×10^{-4}	$HS^-_{(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + S^{2-}_{(aq)}$	sulfide ion	
	water (55.5 mol/L)	1.8×10^{-3}	$H_2O_{(\ell)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + OH^-_{(aq)}$	hydroxide ion	
	hydroxide ion	0	$OH^-_{(aq)} + H_2O_{(\ell)} \longleftarrow H_3O^+_{(aq)} + O^{2-}_{(aq)}$	oxide ion	4

Notes:

1. All strong acids are completely reacted and therefore written as $H_3O^+_{(aq)}$ plus the anion of the acid.
2. All negative ions above water on the right side of the equation have essentially no ability to attract protons.
3. The hydronium ion is only listed so that H_2O may appear as a base on the right side of the equation.
4. $O^{2-}_{(aq)}$ does not exist and is written as $OH^-_{(aq)}$.
5. Quantitative acid-base reactions are those involving the reaction of $H_3O^+_{(aq)}$ with any base below the nitrite ion, and the reaction of $OH^-_{(aq)}$ with any acid above the hydrogen sulfite ion.
6. A single arrow is used for equilibriums which are greater than 99% in one direction. In this acid-base table the equilibrium arrows are for the reaction of the 0.10 mol/L aqueous acid with water.
7. Indicators are not used as 0.10 mol/L solutions. The indicators have been empirically placed on the table so approximate reaction predictions can be made.

10. Formulas

$$\underset{e}{n} = \frac{q}{Q} = \frac{It}{9.65 \times 10^4}$$

$$\underset{(kW \cdot h)}{E} = \frac{IVt}{1000}$$

$$\underset{(J)}{E} = IVt$$

11. SI Units & Symbols

metre	m
gram	g
tonne	t
mole	mol
litre	L
second	s
ampere	A
volt	V
coulomb	C
joule	J
kilowatt hour	kW·h
pascal	Pa

12. SI Prefixes

Prefix	Symbol	Factor
exa	E	10^{18}
peta	P	10^{15}
tera	T	10^{12}
* giga	G	10^{9}
* mega	M	10^{6}
** kilo	k	10^{3}
hecto	h	10^{2}
deca	da	10^{1}
deci	d	10^{-1}
** centi	c	10^{-2}
** milli	m	10^{-3}
* micro	μ	10^{-6}
* nano	n	10^{-9}
* pico	p	10^{-12}
femto	f	10^{-15}
atto	a	10^{-18}

** most common
* next most common

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